(^119)Sn N.M.R. Studies of the reactions of some organotin(IV) compounds

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^{119}Sn N.M.R. STUDIES OF THE REACTIONS OF SOME ORGANOTIN(IV) COMPOUNDS

by

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December

1980

To mum, dad, and grandparents.

Declaration

The work described in this thesis was carried out in the University of Durham between October 1979 and September 1980. This work has not been submitted, either completely or in part, for a degree in this or any other University and is the original work of the author except where acknowledged by reference.

Acknowledgements

I should like to express my thanks to Dr. K.B. Dillon for his excellent supervision and unfailing encouragement, throughout the course of this work. I should also like to thank Mr. R. Coult for the large number of elemental analyses he performed, Mrs. M. Cocks for the microanalyses, and Dr. A. Royston for his work on the ^{119}Sn and ^{11}B n.m.r. instrumentation and for his readily available advice on problems of a technical nature.

The comments (and occasional helpful suggestions) from other members of the research group, namely J. Lincoln, A.W.G. Platt, R.M.K. Deng, and A. Marshall are acknowledged. Thanks are also due to Dr. Sheena Bartlett for typing this thesis, and the provision of a maintenance grant from Durham University is gratefully acknowledged.

Abbreviations Used in This Thesis

py	=	pyridine, C_5H_5N
phen	=	1,10-phenanthroline, $C_{12}H_8N_2$
dipy	=	2,2'-dipyridyl, $C_{10}H_8N_2$
D.M.S.O.	=	dimethylsulphoxide
Me	=	methyl
Et	=	ethyl
Pr	=	n-propyl
Bu	=	n-butyl
Pe	=	n-pentyl

Abstract

The chemistry of some organotin(IV) halides, and in particular their acceptor properties in solution, has been investigated by ^{119}Sn n.m.r. spectroscopy. Mono- and di-organotin(IV) chlorides and bromides were found to coordinate either one or two halide ions whereas tri-organotin(IV) halides would coordinate only one. The tetraorganotin(IV) species showed no acceptor properties whatsoever, even in solution. The complexes thus formed were isolable, and could therefore be investigated by other conventional techniques.

Reactions between organotin(IV) chlorides and the powerful Lewis acids, $SbCl_5$ and BCl_3 were investigated in solution by ^{119}Sn and ^{11}B (where appropriate) n.m.r. spectroscopy. Exchange between organo-groups from the organotin(IV) compound and chloride ions from the Lewis acid occurred in most cases, and interesting series of chemical shifts were obtained.

Solution ^{119}Sn n.m.r. spectroscopy was also used to investigate the reaction between organotin(IV) chlorides and the acidic solvent systems, 100% H_2SO_4, 25-oleum, and chlorosulphuric acid. Although other conventional techniques could not be employed to assist product identification, the chemical shifts obtained were very informative, and in the majority of cases could be rationalised on the basis of the reactions expected in these solvents.

Several solid adducts were prepared from reactions between organo-tin(IV) chlorides and the pyridine bases, pyridine, dipy, and phen. Although the adducts themselves were easily prepared , results from ^{119}Sn n.m.r. solution (or solid-state) investigations proved generally disappointing. This was due to the very low solubility of the adducts even in solvents of quite high polarity, and probably to relaxation-time problems in solid-state n.m.r.

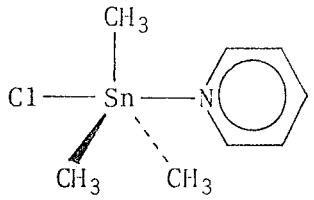
Chapter 1 INTRODUCTION

1. Coordination chemistry of Organotin(IV) halides

There are many examples known of the coordination of both neutral ligands[1-8] and anionic unidentate halide ligands[9-12] to tin(IV) halides and organotin(IV) halides,[1-12] e.g. $SnCl_4$.phen,[2] $SnCl_6^{2-}$, Me_2SnCl_2.dipy,[1] $Me_2SnCl_4^{2-}$,[12] $Ph_3SnCl_2^-$,[8] $SnCl_5^-$,[45,48] Me_3SnCl.py.[1,2] The resulting six-coordinate complexes possess octahedral structures and the five-coordinate complexes have trigonal bipyramidal geometries.

During the past 15 years there has been considerable interest in the behaviour of tin(IV) halides and organotin(IV) halides[1,2,13] as Lewis Acids, with the tin atom acting as an acceptor for 1 or 2 electron pairs, thus increasing its coordination from 4 to 5 or 6 by the addition of bases (such as py, dipy, phen) or halide ion. Amongst the organotin halides, reactivity as Lewis Acids varies in the following manner. Tin tetraalkyls and tetraaryls show no Lewis acidity, whereas tin(IV) halides are strong Lewis acids, forming adducts with a wide variety of bases. In solution in non-donor solvents, tin(IV) chloride will form solid 1:2 adducts with unidentate heterocyclic bases (e.g. pyridine) and 1:1 adducts with bidentate bases (e.g. dipy, phen).[14,15] The organotin halides R_nSnX_{4-n} are intermediate in Lewis acidity between R_4Sn and SnX_4, with acidity generally increasing as the halide proportion increases. For example, trimethyltinchloride forms a 1:1 adduct with pyridine shown by X-ray analysis[16] to have trigonal bipyramid stereochemistry with trans, apical N and Cl atoms (see fig. 1).

Fig. 1 Structure of $Me_3SnCl.py$



Equilibrium studies in carbon tetrachloride[17] have shown that trimethyltinchloride is only a weak Lewis acid. Reaction with phen or dipy under similar conditions results in no compound formation,[1] thus the tin atom in trimethyltinchloride will only increase its coordination to 5 under normal circumstances.

Solid 1:2 adducts[13] have been isolated, however, from the reaction of the halides R_2SnX_2 (R = alkyl or aryl) with unidentate, heterocyclic bases (e.g. pyridine), as have 1:1 adducts with dipy and phen.[1-8] Mössbauer, dipole moment, and n.q.r. studies[18] of the adducts $R'RSnCl_2.2B$ (B = mono- or bidentate base) have shown that the R groups are trans and the chlorine atoms are cis in octahedral complexes; two cis unidentate base molecules may be replaced by one molecule of a bidentate base.

Similar reactions to those outlined for R_2SnX_2 occur with $RSnX_3$. For example, $MeSnCl_3$ forms a 1:2 complex with pyridine, or 1:1 complexes with phen or dipy.[1,2,7]

All of the neutral adducts referred to above have been well characterised in the past, mainly by infra-red, Raman, and Mössbauer spectroscopy, but only in a few limited cases has ^{119}Sn n.m.r. been applied.[19,20,21]

The formation of anionic adducts by reaction of organotin(IV) halides with tetraalkylammonium chlorides (or bromides) has also been investigated previously.[9-12] A similar situation to that for

neutral adduct formation exists, in that trialkyl (or aryl) tin chlorides will add only one chloride ion under normal circumstances, forming the 5-coordinate organotin complex $R_4N^+R'_3SnCl_2^-$. The mono- or di-alkyl (or aryl) tin chlorides can add either one or two chloride ions, depending on the reaction conditions. For example (ref. 9).

$$\underset{8.68\ \text{mmol}}{Me_4NCl} + \underset{8.72\ \text{mmol}}{Ph_2SnCl_2} \longrightarrow [Me_4N^+]\ [Ph_2SnCl_3^-]$$

$$\underset{6.05\ \text{mmol}}{Me_4NCl} + \underset{2.91\ \text{mmol}}{Ph_2SnCl_2} \longrightarrow [Me_4N]_2\ [Ph_2SnCl_4]$$

Thus, depending on the ratios of starting materials, both 5- and 6-coordinate anionic complexes can be formed, which should be readily distinguishable by use of ^{119}Sn n.m.r. spectroscopy.

2. Present Work

The purpose of the work was to investigate by use of ^{119}Sn n.m.r., and conventional techniques, some addition reactions of organotin halides, R_nSnX_{4-n} where R = phenyl or methyl, X = chloride or, in a few cases, bromide. Although the starting materials used (4-coordinate organotin halides) have been thoroughly investigated by ^{119}Sn n.m.r.,[22] relatively little work has been done on the adducts resulting from reaction of these compounds with halide ion, or uni- or bidentate Lewis bases, such as pyridine, dipy or phen, as shown in Table 1.

TABLE 1 Some previously recorded ^{119}Sn n.m.r. chemical shifts of compounds relevant to this work

Compound	Solvent	[a]Shift (ppm)	Reference
$Me_2SnBr_2.dipy$	satd.CH_2Cl_2	+245	20
$Me_3SnCl.py$	$CHCl_3$	+ 25.4	19
$(MeSnCl_5)^{2-}$	H_2O	+464	21
$(MeSnBr_3Cl_2)^{2-}$	H_2O	+543	21
$(Et_4N)^+(Me_3SnCl_2)^-$	satd. Me_2CO	+ 53	20
$(Me_3Sn.dipy)^+(BPh_4)^-$	CH_2Cl_2	+ 18	20

[a] These, and all subsequent ^{119}Sn chemical shifts are expressed relative to external tetramethyltin as reference, the upfield direction being taken as positive.

The high field shifts relative to the 4-coordinate parent compounds are indicative of increased coordination about the ^{119}Sn atom.

(i) Formation of anionic complexes by halide addition

The reaction between organotin halides (halide = Cl^- or Br^-) and Cl^- or Br^- respectively, in a non-polar organic solvent has been investigated. Variation of ^{119}Sn chemical shift with addition of increasing amounts of halides was monitored and recorded graphically. Isolation of 1:2 (or 1:1 where appropriate) addition complexes was undertaken, the products being investigated by elemental analysis, infra-red, and Raman techniques as well as ^{119}Sn n.m.r. and ^{35}Cl n.q.r. spectroscopy.

(ii) Reaction with Lewis Acids: $SbCl_5$ and BCl_3

It was anticipated that Cl^- abstraction from the organotin chloride by $SbCl_5$ or BCl_3 would occur in at least some cases, resulting in a cationic chloroorganotin(IV) species as follows:

$$R_nSnCl_{4-n} + \begin{matrix} SbCl_5 \\ \text{or} \\ BCl_3 \end{matrix} \longrightarrow R_nSnCl_{3-n}^+ + \begin{matrix} SbCl_6^- \\ \text{or} \\ BCl_4^- \end{matrix}$$

The detection of a cationic, 3-coordinate tin complex should be straightforward by ^{119}Sn n.m.r. since the resulting complex would be highly deshielded with respect to the parent compound, and hence give a signal at much lower field.

In practice, the above reaction was observed not to take place; instead, exchange between chloride and R groups occurred, giving products which could be identified in solution by ^{119}Sn n.m.r. and, in the case of BCl_3 reactions, by ^{11}B n.m.r. Thus the organotin chlorides underwent exchange reactions with $SbCl_5$ and BCl_3, and an interesting series of trends was obtained.

(iii) Reactions in Acidic Solvents

^{119}Sn n.m.r. chemical shifts of all (initially) 4-coordinate organotin chloride starting materials, plus a few related 5- and 6-coordinate complexes were recorded in the following three acidic solvents: 25-oleum, 100% sulphuric acid, and chlorosulphuric acid. The reactions which might occur are potentially quite complex (sulphonation, solvolysis, chlorination, hydrolysis, etc.), and in several cases, ^{119}Sn n.m.r. spectra containing several peaks were obtained. Almost without exception, the 4-coordinate species gave shifts in these solvents at higher field, indicating an

increase in coordination of the tin atom.

(iv) Formation of neutral 5- and 6-coordinate adducts

Reactions were carried out between 1:1 or 1:2 stoichiometric ratios of organotin halide and the donor ligands pyridine, 1,10-phenanthroline, and 2,2'-dipyridyl, in various non-coordinating solvents. The resulting products were, in most cases, very insoluble white solids, precipitating out of solution immediately on mixing. Elemental analysis, infra-red, and Raman investigations were carried out as a means of checking that product formation had occurred, since the majority of the products were already well known.[1-8] Because of the very low solubilities of most of the products (with the exception of the 5-coordinate, $R_3SnCl.py$ complexes) ^{119}Sn n.m.r. spectra were difficult to obtain, requiring long overnight runs, or even over complete weekends in some cases.

3. Techniques Used

(i) ^{119}Sn n.m.r. spectroscopy[22-32]

Elemental tin has three isotopes with non-zero spin and magnetic moments, the isotopes ^{115}Sn, ^{117}Sn and ^{119}Sn. The only isotope to be successfully studied by n.m.r. is ^{119}Sn, however, since ^{115}Sn has too low a natural abundance, and ^{117}Sn produces resonances which are weaker and therefore less suitable for study. ^{119}Sn has the advantage of having a parent radioisotope, ^{119m}Sn, and is therefore suitable for study by Mössbauer spectroscopy.

The main limitations of ^{119}Sn n.m.r. spectroscopy are twofold; firstly the natural abundance of the ^{119}Sn isotope in elemental tin is only 8.7%, and secondly the sensisivity of the ^{119}Sn isotope is only 5% that of the proton.

The lack of sensitivity may be partially overcome by using 8.4 mm diameter n.m.r. tubes instead of the 5 mm tubes used in proton n.m.r. but even so, the signal is not visible on a single scan of the spectrum. Signal enhancement can be conveniently achieved by signal averaging, using a computer of average transients. This involves utilization of F.T. as opposed to C.W. n.m.r., since with the former technique, a large number of scans can be accumulated in a relatively short time.

^{119}Sn n.m.r. spectroscopy is, despite the technical problems involved, ideally suited for the study of changes of coordination in tin(IV) compounds, since ^{119}Sn chemical shifts cover a range greater than 1800 ppm. The main factors which influence chemical shift[22] are the coordination number about tin, substituent effects in the organotin halide series R_nSnX_{4-n}, and isotope effects, although the latter have been shown to be negligible in most cases.[23]

The interaction of an organotin(IV) halide with a coordinating solvent may cause the ^{119}Sn chemical shift[19,26,27] to appear at much higher field, since increased coordination to 5 or 6 about tin causes an upfield shift. Hence choice of solvent is important when recording ^{119}Sn chemical shifts. Hunter and Reeve[19] have shown that the dilution of Me_3SnCl with non-coordinating solvents like benzene or carbon tetrachloride has only a slight effect on the chemical shift and therefore no complexing with the solvent or self-association occurs in this case. Shifts of Me_3SnCl in carbon tetrachloride are also essentially independent of both temperature and concentration. Polar solvents such as acetone, D.M.S.O., or pyridine, however have been shown to cause large variations in chemical shift which are also dependent on concentration. For example, the shift of Me_3SnCl changes from -159 ppm to +9 ppm as the mole ratio of

pyridine is increased from 1:0 to 1:12, the greatest change occurring between 1:0 and 1:1, consistent with the formation of a 5-coordinate, trigonal bipyramid adduct. Also, the shift of Me_2SnCl_2 in D.M.S.O. (+246 ppm) is nearly 400 ppm to high field of the parent compound, Me_2SnCl_2, corresponding to formation of a 6-coordinate, octahedral complex, $Me_2SnCl_2.2DMSO$.[20] Some examples of the effect of changes in coordination number on chemical shifts are shown in Table 2.

TABLE 2 Examples of the effect of coordination number on ^{119}Sn chemical shifts[22]

Compound	[a] ^{119}Sn chemical shift (ppm)	Geometry of the atom	% s-character in Sn-C bond
Me_2SnCl_2	-137	tetrahedral R_2SnX_2	25
$Me_2Sn(SCSNEt_2)Cl$	+204	trig. bipyr. cis-R_2SnX_3	33
$Me_2Sn(SCSNEt_2)_2$	+336	octahedral trans R_2SnX_4	50
Me_3SnCl	-155.1	tetrahedral R_3SnX	25
$Me_3SnCl.DMSO$	+ 86	trig. bipyr. R_3SnX_2	33

[a] Solvent CH_2Cl_2 in all cases.

The other major factor to affect ^{119}Sn n.m.r. chemical shifts is the substituent effect of R and X in the organotin halide compounds,[19,34,35] for example, the 4-coordinate R_nSnX_{4-n} series, where R = alkyl or aryl, X = halogen.

The effect of changing R is generally that as the electron-releasing power of R increases, the tin atom becomes progressively more shielded, and therefore chemical shifts should move to higher field (see Table 3).

Taft constants for the organic group are probably a better guide to polar effects than electronegativity, since replacing an alkyl by a phenyl group causes a shift to high field, inconsistent with the greater electron-withdrawing power of a phenyl group.

TABLE 3 ^{119}Sn Chemical Shifts (ppm) for alkyl- and phenyltin chlorides

R Group	$RSnCl_3$	R_2SnCl_2	R_3SnCl	Taft Constant σ^* (R)
Me	-20	-141	-164	0.000
Et	- 6.5	-126	-155	-0.100
nBu	- 6.0	-122	-141	-0.130
tBu	-	- 52	-	-0.225
Ph	+63	+ 32	+ 48	+0.600

The upfield shift may therefore be due to increased polarisability of these substances.

Changing the group X also affects the chemical shift of tin(IV) compounds. For example, in the series R_3SnX, the shift moves to lower field with increased inductive withdrawing power of X.[32]

As previously mentioned, isotope effects can be neglected in most cases when discussing ^{119}Sn n.m.r. chemical shifts. The only other factor likely to influence shifts is temperature; organotin compounds complexed with polar solvents or auto-associated usually show a low field shift as temperature increases, allowing calculation of ΔH values. Since all measurements for the purposes of this thesis were carried out at constant temperature, however

this effect can be neglected.

(ii) Infra-red Spectroscopy

The main region of interest in the infra-red spectrum is between 200 and 650 cm^{-1}, since almost all tin-halogen and tin-carbon stretching frequencies occur within this range. The strength of these bands varies from compound to compound but in most cases they are strong enough to be readily identified. The positions of the bands are very characteristic of the different organotin halide compounds encountered, and the spectra of most of these compounds are well documented in the literature.[1-12,36] Infra-red spectroscopy therefore provides a quick, convenient method of checking reaction products by a 'fingerprinting' technique, and also as a check on whether any starting material remains in the product after isolation. Unfortunately, the spectrometers available had cut-off frequencies of 250 cm^{-1}, hence this was the lower limit of all spectra run.

TABLE 4 Characteristic i.r. frequencies for Sn-Cl and Sn-C stretches in starting materials (250 cm^{-1} - 650 cm^{-1})

Compound	ν(Sn - C)	ν(Sn - Cl)	ref.
Ph_4Sn	270, 263 cm^{-1}	-	36
Ph_3SnCl	274 - 265 cm^{-1}	346 - 338 cm^{-1}	36
Ph_2SnCl_2	274 - 279 cm^{-1}	364, 356, 350 cm^{-1}	36
$PhSnCl_3$	250 cm^{-1}	385 - 364 cm^{-1}	36
Me_4Sn	528 cm^{-1}	-	2
Me_3SnCl	524, 513 cm^{-1}	331 cm^{-1}	2
Me_2SnCl_2	560, 542 cm^{-1}	361, 356 cm^{-1}	2
$MeSnCl_3$	551 cm^{-1}	382, 368 cm^{-1}	2
$SnCl_4$	-	407 cm^{-1}	2

Although the region between 650 cm^{-1} and 250 cm^{-1} is in general free from C-H and C-C absorptions, bands in this region also arise from the internal vibrations of ligands such as pyridine, dipy, or phen. The positions of these bands, however, only vary slightly from compound to compound, and can usually therefore be readily assigned in any given spectrum.

For the complexes prepared by halide addition, different counter ions were used in some cases, yet the frequencies of the anion peaks were observed to vary only slightly with different tetraalkylammonium counter ions. Infra-red spectroscopy therefore provides a means of confirming the presence of similar species in the complexes.

(iii) Raman Spectroscopy

This technique was used in conjunction with infra-red as a means of confirming that reactions had taken place by comparison of product spectra with those of starting materials. Spectra were run from 1000 cm^{-1} down to 100 cm^{-1}, but only the region between 150 cm^{-1} and 650 cm^{-1} is of real interest, since below 150 cm^{-1}, many of the low frequency bending modes occur which only complicate the picture. Raman spectroscopy is also useful for looking at vibrations which are both i.r. and Raman active, but which occur below 250 cm^{-1} in the infra-red.

TABLE 5 Raman spectra of Organotin Chloride starting materials, (150 cm^{-1} - 700 cm^{-1})

Compound	Bands (cm^{-1})	Ref.
Ph_4Sn	207, 264, 616, 657	37
Ph_3SnCl	214, 270, 329, 618, 656	37
Ph_2SnCl_2	188, 214, 225, 237, 335, 350, 657	-
$PhSnCl_3$	184, 215, 249, 300, 363, 383, 612, 660, 687	39
Me_3SnCl	150, 318, 518, 548	40
Me_2SnCl_2	312, 411, 458, 516, 568	38
$MeSnCl_3$	352, 370, 522, 546	38

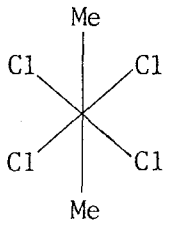
(iv) ^{35}Cl n.q.r. (Nuclear quadrupole resonance spectroscopy)

Although this would appear to be a potentially extremely useful technique for obtaining structural information in the solid state for all Cl^- containing organotin compounds, at present it has severe experimental disadvantages in its application. The technique is only applicable to the solid state and is particularly sensitive to imperfections or strains in the crystal structure, or to slightly impure samples. In many compounds the technique is too insensitive to detect signals, and this turned out to be the case for the great majority of compounds studied within this thesis.

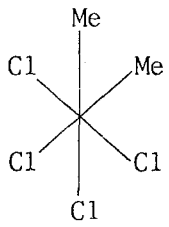
N.q.r. signals occur at resonances between the non-degenerate energy levels of a nuclear quadrupole interacting with an assymetric electric field gradient. Thus for completely symmetrical chloride ion no absorption is found. A chlorine atom produces a ^{35}Cl ($I = \frac{3}{2}$) resonance at 54.87 MHz. Chlorines in other molecular environments have resonances between 54.87 and 0 MHz, depending on the character

of the X-Cl bond. Each chemically distinct chlorine gives a separate signal, and in addition, crystallographic inequivalencies may further split these lines.

Therefore it is theoretically possible to distinguish between certain isomers in the solid state by use of n.q.r. techniques. For example, for octahedral $Me_2SnCl_4^{2-}$ where the methyl groups are mutually trans, all other chlorines are equivalent and only 1 group of lines should be observed in the ^{35}Cl n.q.r. spectrum. If the methyls are cis, the chlorines will be in 2 chemically distinct pairs, and two groups of lines of approximately equal intensity are then expected in the spectrum i.e.



trans-$Me_2SnCl_4^{2-}$



cis-$Me_2SnCl_4^{2-}$

The characteristic ^{35}Cl n.q.r. frequencies of the organotin chlorides starting materials are listed in Table 6 (all measurements refer to 77K).

TABLE 6 ^{35}Cl n.q.r. frequencies of Organotin(IV) chlorides

Compound	^{35}Cl n.q.r. Frequencies (MHz)	Ref.
Ph_3SnCl	13.66, 16.750, 16.985	41
Ph_2SnCl_2	15.764, 15.623, 15.523, 15.495	43
$PhSnCl_3$	21.291, 20.592, 20.097	43
Me_3SnCl	11.40	42
Me_2SnCl_2	15.466	41
$MeSnCl_3$	21.85, 19.43	41
$SnCl_4$	23.720, 24.140, 24.226, 24.296	41

Chapter 2 EXPERIMENTAL

1. Methods Used

(i) Glove box techniques

The vast majority of reactions were carried out in an atmosphere of dry nitrogen, due to the moisture sensitivity of many of the products and starting materials. All starting materials (except tetraphenyltin and triphenyltinchloride) and products other than neutral adducts of dipy or phen were also stored under nitrogen in closed sample bottles.

Reactions were performed in a glove box which was continuously purged with dry nitrogen. The box was equipped with two entry ports; a large port, which required purging for 30 mins before opening to the glove box, and a smaller 'quick-entry' port. The latter was evacuated by flushing with nitrogen by means of the excess pressure in the glove box. Furthermore, a dish of phosphorus pentoxide was kept in the glove box to remove final traces of water. The surface of the phosphorus pentoxide was reformed each time a skin developed. An external vacuum line was connected to the glove box so that filtering and pumping operations could be carried out completely within the box.

The vacuum line was also used for drying purposes, and for carrying out reactions involving boron trichloride. The line was equipped with a rotary pump.

All moisture sensitive materials were weighed outside the glove box in stoppered sample bottles.

(ii) Preparation of starting materials

(a) Organotin(IV) compounds

Ph_4Sn, Me_3SnCl, and $MeSnCl_3$ were purchased from Pierce and Warriner; Ph_3SnCl was purchased from Cambrian Chemicals Ltd; Ph_2SnCl_2, Me_2SnCl_2, and $SnCl_4$ were purchased from BDH Lab. Reagents Ltd, $PhSnCl_3$ was purchased from Pfaltz and Bauer Ltd; Me_4Sn was purchased from Aldrich Chemical Co. Ltd; and Me_2SnBr_2 was purchased from Alfa Products Ltd. All were used without further purification, after no impurities had been detected by spectroscopic techniques (i.e. infra-red or ^{119}Sn n.m.r. where appropriate).

The compounds (b) and (c) were both prepared by an adaptation of a literature method (ref. 2).

(b) Triphenyltinbromide

This was prepared by the following procedure. An excess of solid sodium bromide was added to an acetone solution containing triphenyltinchloride. The mixture was then refluxed, with continuous stirring, for 3 hours. The resulting mixture was then filtered, to remove undissolved sodium bromide and sodium chloride, then the crude product isolated by removing the solvent. The pure product was obtained as white crystals by recrystallization from a hexane/chloroform mixture. A ^{119}Sn n.m.r. of the product dissolved in methylene chloride yielded a single peak at +60.5 ppm (cf. shift of triphenyltinchloride in methylene chloride is +48 ppm).

Typical analyses: C, 50.8; H, 3.9; Br, 19.7%

Ph_3SnBr requires C, 50.2; H, 3.5; Br, 18.6%

(c) Trimethyltinbromide

This compound was prepared by the same method as that for triphenyltinbromide. An excess of sodium bromide was added to an acetone solution of trimethyltinchloride, then the mixture was

refluxed, with stirring, for 3 hours. After filtering of the solid residue (unreacted sodium bromide, and sodium chloride product), the resulting liquid was pumped on the vacuum line, with several additions of 30 - 40° petroleum ether to ensure complete removal of solvent. A white solid residue remained in the flask which melted to an orange liquid at room temperature. A ^{119}Sn n.m.r. spectrum of the product yielded a single peak at -131.5 ppm in good agreement with the literature value[22] of -130.7 ppm for Me_3SnBr.

(d) Lewis acids

Antimony pentachloride and boron trichloride were purchased from BDH Lab. Reagents Ltd. and used without further purification.

(iii) Ligands

Pyridine was supplied by BDH Lab. Reagents Ltd., and before use was stored over molecular sieve, within the glove box for several days, or for reaction with particularly moisture-sensitive starting materials, was distilled and stored over potassium hydroxide. 2,2'-Dipyridyl was used as supplied (Koch-Light Ltd.). 1,10-Phenanthroline was obtained anhydrous (Aldrich Chemical Co. Ltd.) and was used without further purification.

(iv) Adducts

(a) Nitrogen bases

The formation of adducts with pyridine, phen, and dipy occurred very rapidly in all cases, and with the exception of the 1:1 adducts formed between trimethyl- or triphenyltinchlorides with pyridine, all products were very insoluble in the common organic solvents used in the preparations, being deposited as dense,

amorphous white solids. This was advantageous in that any excess of either starting material would be removed during the washing process, but low solubility created many problems during ^{119}Sn n.m.r. investigations, and the fact that powders, rather than crystals, formed meant a more strained crystal structure which is unfavourable for ^{35}Cl n.q.r. spectroscopy. The 1:1 adducts formed between pyridine and trimethyl- or triphenyltinchloride were soluble in non-polar organic solvents, and adduct formation could thus be monitored by ^{119}Sn n.m.r. spectroscopy. Once reaction had been established, the solid adducts were isolated by pumping off all traces of solvent on the vacuum line. The solid 5- and 6-coordinate adducts were air-stable once formed, and hence could be stored outside the glove box, with no sign of any decomposition.

Since the type of reactions performed resulted in little or no hydrogen chloride vapour building up within the glove box, reactions with pyridine could be carried out without using a closed system, since there were few problems with white fumes of pyridinium chloride. Pyridine vapour was removed from the glove box atmosphere by means of a recirculation pump system.

Care was taken not to handle moist phen or dipy complexes with metal spatulas, since the ligands were found to form bright red complexes on attacking the metal, which contaminated the product.

(v) Solvents

Methylene Chloride

This was stored over mesh 4A molecular sieve under nitrogen, otherwise used as supplied.

30 - 40° Petroleum Ether

This was used as supplied, to wash and dry complexes, since almost all products were found to be insoluble in this solvent.

Other solvents used in this work were the best available commercial grades and were used without further purification. These included benzene, carbon disulphide, chloroform, carbon tetrachloride, and acetone. All were stored over mesh 4A molecular sieve, under nitrogen.

(vi) Analyses

Carbon, hydrogen, and nitrogen were determined as a laboratory service by microcombustion with a Perkin-Elmer 240 Elemental Analyser. The reliability of the machine was variable.

Chlorine was determined by potentiometric titration. A suitable aliquot was titrated against N/100 silver nitrate solution using Ag,AgCl electrodes in an acetone medium.

Both tin and antimony were determined by the same method; samples were decomposed by acid until water soluble, then elemental percentages were determined by atomic absorption.

2. ^{119}Sn nuclear magnetic resonance spectroscopy

^{119}Sn nuclear magnetic resonance spectra were obtained using a PDP 11/34 computer with 64K memory and RT-11 operating system, constructed in this department by Dr. A. Royston. Attached to the computer are the following devices:-

a) 2 RX01 floppy discs

b) HIPLOT digital plotter

c) oscilloscope for displaying data held in computer

d) pulse programmer to control timing functions in the system

e) DECWRITER LA 36 monitor typewriter.

The aim of the system is to store and accumulate the free induction decay produced by a powerful R.F. pulse. After the required number of scans have been completed, the computer processes the accumulated F.I.D.s to give the spectrum. The sweep width can be varied from 126 Hz to 20 KHz (a maximum width of ~900 ppm is available to observe resonances in the range -200 to +900 ppm).

The timing of the R.F. burst is controlled by a pulse programmer, which in turn is operated entirely by software. Pulse sequence parameters are entered from the teletype. There can be up to 15 pulses with lengths of 1 to 31 μs, in the cycle, with any interval in the range 0.1 to 25.5 secs. The transmitter frequency is provided by a Racal 9061/2 frequency synthesiser, which is controlled by the computer.

The output of a crystal oscillator is directed to two parts of the apparatus; firstly to a switch operated by the pulse programmer, and thence to a 100W amplifier connected to the sample probe; secondly to a phase detector which is part of the signal detection system.

Essentially the sample probe consists of a circuit tuned to the ^{119}Sn n.m.r. frequency, with the sample contained within an inductor placed in the pole gap of a Perkin-Elmer R10 permanent magnet (1.4T).

An R.F. burst across the inductance causes the ^{119}Sn nuclei to precess; relaxation induces a small R.F. voltage across the coil. After amplification, these n.m.r. frequencies are mixed with the original input to the R.F. gate to give an interferogram. After filtering and further amplification, the signal is digitised into (normally) 512 regularly spaced samples before being stored in the computer memory.

Spectra were run at 307.2K, the stationary samples being contained in 8.4 mm external diameter n.m.r. tubes, and all chemical shifts measured relative to an external reference of tetramethyltin, with the upfield direction taken as positive.

3. ^{11}B n.m.r. spectroscopy

The same computer system was used for obtaining ^{11}B n.m.r. spectra; the only slight modifications required were changing the probe and typing in a user command via the teletype. Shifts were measured relative to external trimethylborate and results have been expressed relative to this standard. The ^{11}B chemical shift of $BF_3.Et_2O$, the other main ^{11}B reference material, has been reported as +18.75 ppm relative to $(MeO)_3B$.[44] The upfield direction is again taken as positive.

4. Other Spectroscopic Techniques

(i) Infra-red Spectroscopy

Infra-red spectra of solids were run as nujol mulls, from 4000 cm^{-1} to 250 cm^{-1} using a Perkin-Elmer 457 grating spectrometer, the nujol being stored over sodium. Tinchloro- (or bromo-) compounds were found to attack unprotected caesium iodide plates, which were necessary to give spectra to 250 cm^{-1}. The plates were therefore protected by polythene sheets (giving absorptions below 1000 cm^{-1} at 712 and 722 cm^{-1}). Except where otherwise stated, all spectra were run at a medium scan rate (18 mins over the range 4000 to 250 cm^{-1}).

(ii) Raman Spectroscopy

Raman spectra were recorded by Mrs. J. Slegrova on a Cary 82 spectrometer using an argon laser.

(iii) ^{35}Cl nuclear quadrupole resonance

N.q.r. spectra were recorded on a Decca spectrometer, usually in 16 mm external diameter ampoules, at liquid nitrogen temperature. Zeeman modulation was used throughout. Resonant frequencies were determined within an accuracy of ±10 KHz by interpolation between the spectrometer frequency markers, which were calibrated by means of a frequency counter. Due to probable thermal instability at elevated temperatures, annealing of the samples was not attempted.

Chapter 3 FORMATION OF HALIDE ADDUCTS: REACTIONS WITH TETRAALKYL-AMMONIUM CHLORIDES AND BROMIDES

1. Introduction

Most of the adducts from reaction between organotin(IV) halides and halide ion are well known in the literature,[3,12,29,31,45-50] many having already been well-characterised by techniques such as infra-red, Raman, or Mössbauer spectroscopy. The adducts formed reflect the decrease in Lewis acidity of the organotin(IV) halides as the number of organo-groups is increased from 0 to 4. Hence under normal circumstances tetramethyltin does not react with chloride ion, trimethyltinchloride forms only the 1:1 complex $[Me_3SnCl_2]^-$, but dimethyltindichloride, methyltintrichloride, and tin tetrachloride will add either one or two chloride ions, depending on the molar ratios of starting materials, forming five- or six-coordinate complex anions. Previously isolated examples of each type of adduct, together with literature references are listed in Table 7 (below).

Although only used previously in one or two isolated cases,[20,27] ^{119}Sn n.m.r. is potentially a very useful method for studying the formation of these adducts, both in reacting solutions, and after isolation of the solid products. The latter is facilitated by the ease with which the tetraalkylammonium derivatives dissolve in non-polar solvents, particularly when the alkyl group is large (e.g. n-pentyl). The large upfield shifts observed in the ^{119}Sn n.m.r. spectrum when a 4-coordinate ^{119}Sn atom increases its coordination number from 4 to 5 or 6 means that any adduct formation occurring with halide ion can be readily confirmed and monitored by ^{119}Sn n.m.r. It should be pointed out that it was not known previously whether exchanging systems would

TABLE 7 Previously Isolated Adducts from Reaction of Organotin(IV) Halides with Halide Ion (Halide = Cl^-, Br^-)

Organotin(IV) halide	1:1 Adduct	ref.	1:2 Adduct	ref.
Me_3SnCl	$(Et_4N)[Me_3SnCl_2]$	29,31	-	-
Me_2SnCl_2	$(Et_4N)[Me_2SnCl_3]$	3	$(Et_4N)_2[Me_2SnCl_4]$	31
$MeSnCl_3$	$(Ph_4As)[MeSnCl_4]$	12	$(Et_4N)_2[MeSnCl_5]$	31
Ph_3SnCl	$(Et_4N)[Ph_3SnCl_2]$	3	-	-
Ph_2SnCl_2	$(Ph_4Sn)[Ph_2SnCl_3]$	51	$(pyH)_2[Ph_2SnCl_4]$	47
$PhSnCl_3$	$(Ph_4As)[PhSnCl_4]$	51	$(pyH)_2[PhSnCl_5]$	47
Ph_3SnBr	$[Ph_3P.C_{10}H_{21}][Ph_3SnBr_2]$	48	-	-
$Me_3Sn\ Br$	$(Et_4N)[Me_3SnBr_2]$	45	-	-
Me_2SnBr_2	$(Et_4N)[Me_2SnBr_3]$	3	$Cs_2[Me_2SnBr_4]$	3

be produced on addition of halide, the shift varying with concentration of X^-, or whether separate peaks would be observed for 4-, 5-, and 6-coordinate species. It was also of interest to see whether formation of the 5-coordinate intermediate, in systems where addition of two halide ions is possible, could be detected by ^{119}Sn n.m.r.

2. Present Work

A. In this section of the work, the formation of anionic adducts by reaction of organotin(IV) halides with halide ions (halide = Cl^- or Br^-) was investigated in solution by ^{119}Sn n.m.r. For each system investigated solutions were made up in non-polar solvents from various molar ratios of organotin halide (M) and halide donor (D), the latter in the form of a tetraalkylammonium salt. A portion of each solution was then transferred

to an n.m.r. tube, and the ^{119}Sn n.m.r. spectrum recorded. For any one system, after sufficient samples had been run to obtain a reasonable spread of points from M:D ratios between 1:0 and 1:6, the results were plotted on a graph of chemical shift vs. molar ratio. Solid adducts were also isolated from reactions between 1:1 or 1:2 molar ratios of M and D in non-polar solvents. The adducts formed were characterised by conventional techniques (elemental analysis, infra-red, Raman spectroscopy), and ^{119}Sn chemical shifts in non-polar solvents were also determined. The ^{35}Cl n.q.r. spectrum of each adduct was recorded, but no signals were observed except in the case of $(Et_4N)_2(Me_2SnCl_4)$.

(i) $Me_3SnCl + Et_4NCl$

The variation of ^{119}Sn chemical shift with addition of Et_4NCl (source of Cl^-) was monitored in methylene chloride solvent. The results obtained are listed in Table 8. It should be noted that the likely uncertainty in the measurement of n.m.r. shifts is ±3.5 ppm, this being the difference in ppm between 2 adjacent channels when 512 samples are taken (which was the usual number taken).

When these results were plotted on a graph (Fig. 1), a single stage curve was obtained, which suggests only a one-step reaction, i.e. Me_3SnCl adds only one Cl^- ion, forming the 5-coordinate anionic complex, $[Me_3SnCl_2]^-$.

The white solid product isolated from reaction of a 1:1 molar ratio of starting materials had an infra-red spectrum (Appendix 1, no. 1), in good agreement with that recorded by Davies and Smith[29] for $(Et_4N)[Me_3SnCl_2]$. The Raman spectrum of the product (Appendix 2, no. 1) also clearly differed from that expected from a combination of starting materials, confirming that adduct formation had taken place.

Fig. 1

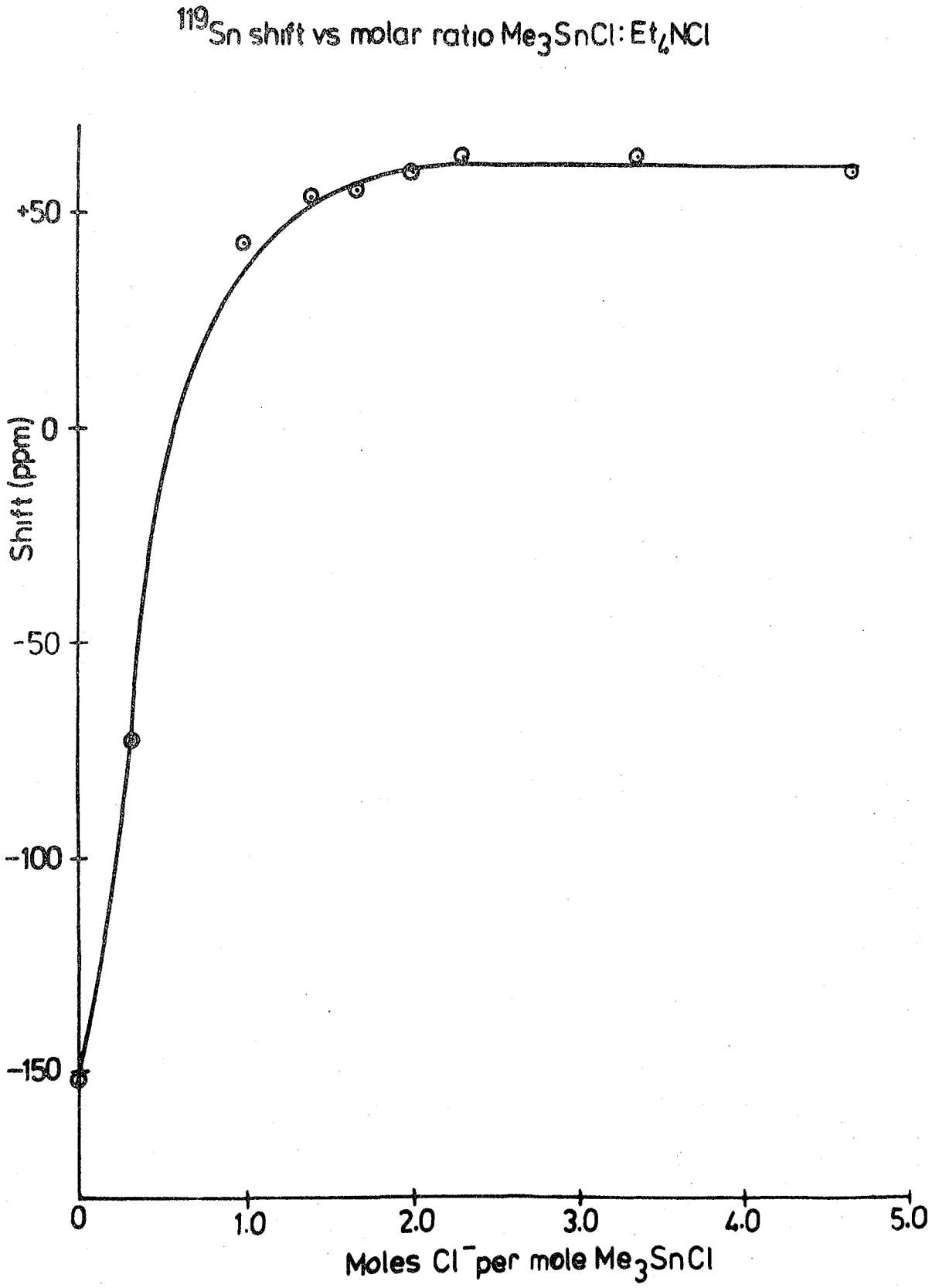

^{119}Sn shift vs molar ratio $Me_3SnCl:Et_4NCl$
+50
0
-50
-100
-150
Shift (ppm)
0
1.0
2.0
3.0
4.0
5.0
Moles Cl^- per mole Me_3SnCl

TABLE 8 Chemical Shift Variation for the Me_3SnCl/Cl^- System

Molar Ratio $Me_3SnCl:Et_4NCl$	^{119}Sn Chemical Shift (ppm)
1:0.00	- 155.1
1:0.31	- 73.3
1:0.98	+ 43.0
1:1.37	+ 53.4
1:1.66	+ 55.3
1:2.00	+ 59.4
1:2.30	+ 62.8
1:3.36	+ 62.8
1:4.66	+ 59.4

In methylene chloride solvent, the ^{119}Sn n.m.r. spectrum of the product yielded a single peak at + 47.7 ppm, which is lower than the limiting shift for $(Et_4N)[Me_3SnCl_2]$, suggesting that partial dissociation occurs in solution.

(ii) $Me_2SnCl_2 + Et_4NCl$

The variation of ^{119}Sn chemical shift with addition of Et_4NCl was monitored in methylene chloride solvent. The results obtained are listed in Table 9.

When these results were plotted on a graph, a two-stage curve was obtained (see Fig. 2), suggesting that a 2-step reaction had occurred, i.e. the stepwise addition of two Cl^- ions, forming initially the 5-coordinate complex, $[Me_2SnCl_3]^-$, then at higher Cl^- concentration, the

Fig. 2

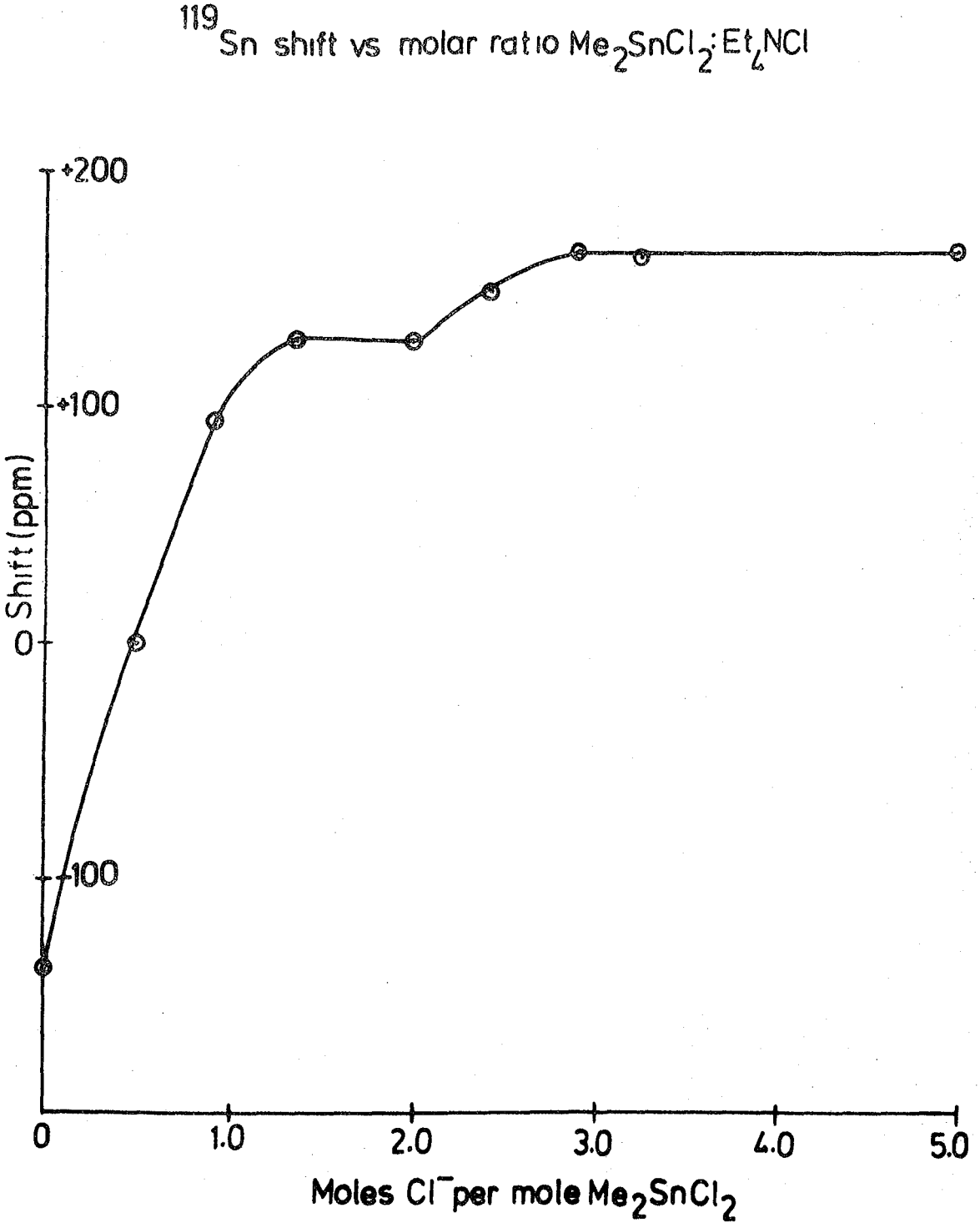

^{119}Sn shift vs molar ratio Me_2SnCl_2:Et_4NCl
+200
+100
0
-100
δ Shift (ppm)
0
1.0
2.0
3.0
4.0
5.0
Moles Cl^- per mole Me_2SnCl_2

TABLE 9 Chemical Shift Variation for the Me_2SnCl_2/Cl^- System

Molar Ratio $Me_2SnCl_2:Et_4NCl$	^{119}Sn Chemical Shift (ppm)
1:0.00	- 137.0
1:0.50	- 0.6
1:0.83	+ 108.2
1:1.31	+ 125.6
1:2.00	+ 128.0
1:2.33	+ 150.1
1:2.95	+ 167.5
1:3.25	+ 164.1
1:5.00	+ 167.8

6-coordinate complex, $[Me_2SnCl_4]^{2-}$. The report that the 5-coordinate complex can be isolated as a tetraalkylammonium salt[3] is clear evidence of its stability.

The white solid product isolated from reaction of a 1:2 molar ratio of starting materials had an infra-red spectrum (Appendix 1, no. 2) closely resembling that recorded in the literature[31] for $(Et_4N)_2[Me_2SnCl_4]$. The Raman spectrum of the product (Appendix 2, no. 2) differed from that expected from a combination of starting materials.

In methylene chloride solvent, the ^{119}Sn n.m.r. spectrum of the product yielded a single peak at + 128.0 ppm. This corresponds closely to the shift expected for the 5-coordinate complex, suggesting a considerable degree of dissociation of the 6-coordinate complex in solution.

The ^{35}Cl n.q.r. spectrum of the product at 77K yielded two signals at 17.522 MHz and 19.576 MHz (see Fig. 3). Two groups of signals suggests cis-methyl groups, since only in this case would there be two pairs of chemically equivalent chlorine atoms.

(iii) $MeSnCl_3$ + Pe_4NCl

The variation of ^{119}Sn chemical shift with addition of Pe_4NCl was monitored in methylene chloride solvent, and for comparison purposes, in chloroform. The results obtained are listed in Table 10.

TABLE 10 Chemical Shift Variation for the $MeSnCl_3/Cl^-$ System

a) Methylene Chloride		b) Chloroform	
Molar Ratio $MeSnCl_3$:Pe_4NCl	^{119}Sn Chemical Shift (ppm)	Molar Ratio $MeSnCl_3$:Pe_4NCl	^{119}Sn Chemical Shift (ppm)
1:0.00	- 18.6	1:0.00	- 21.0
1:0.75	- 195.5	1:0.17	+ 48.9
1:1.26	+ 279.3	1:0.38	+ 97.7
1:1.50	+ 268.8	1:0.65	+ 181.5
1:1.85	+ 352.0	1:1.00	+ 251.8
1:2.13	+ 433.7	1:1.59	+ 265.3
1:3.05	+ 453.8	1:1.93	+ 286.2
1:5.00	+ 481.8	1:2.17	+ 298.5
		1:2.53	+ 314.2
		1:4.60	+ 314.2

Both sets of results when plotted on graphs (see Figs. 4 and 5) yielded two-stage curves, again suggesting the 2-step addition of two

Fig. 3

^{35}Cl Nqr of $(Et_4N)_2(Me_2SnCl_4)_2$

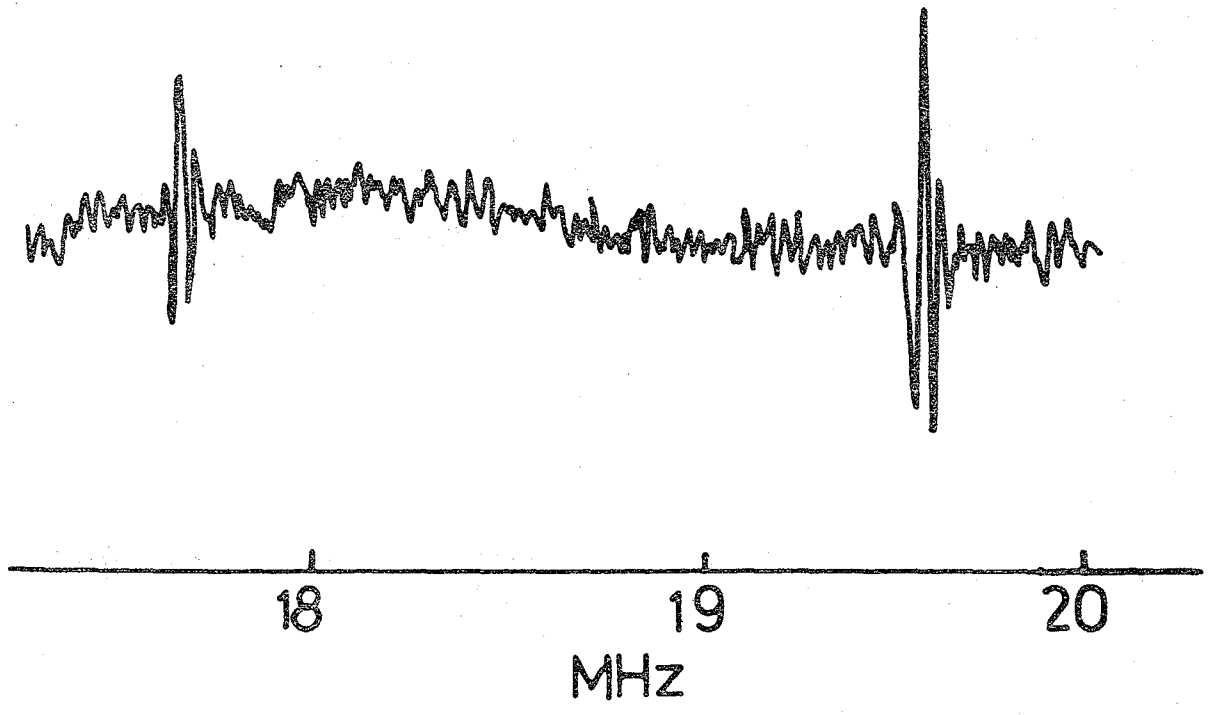


Fig. 4

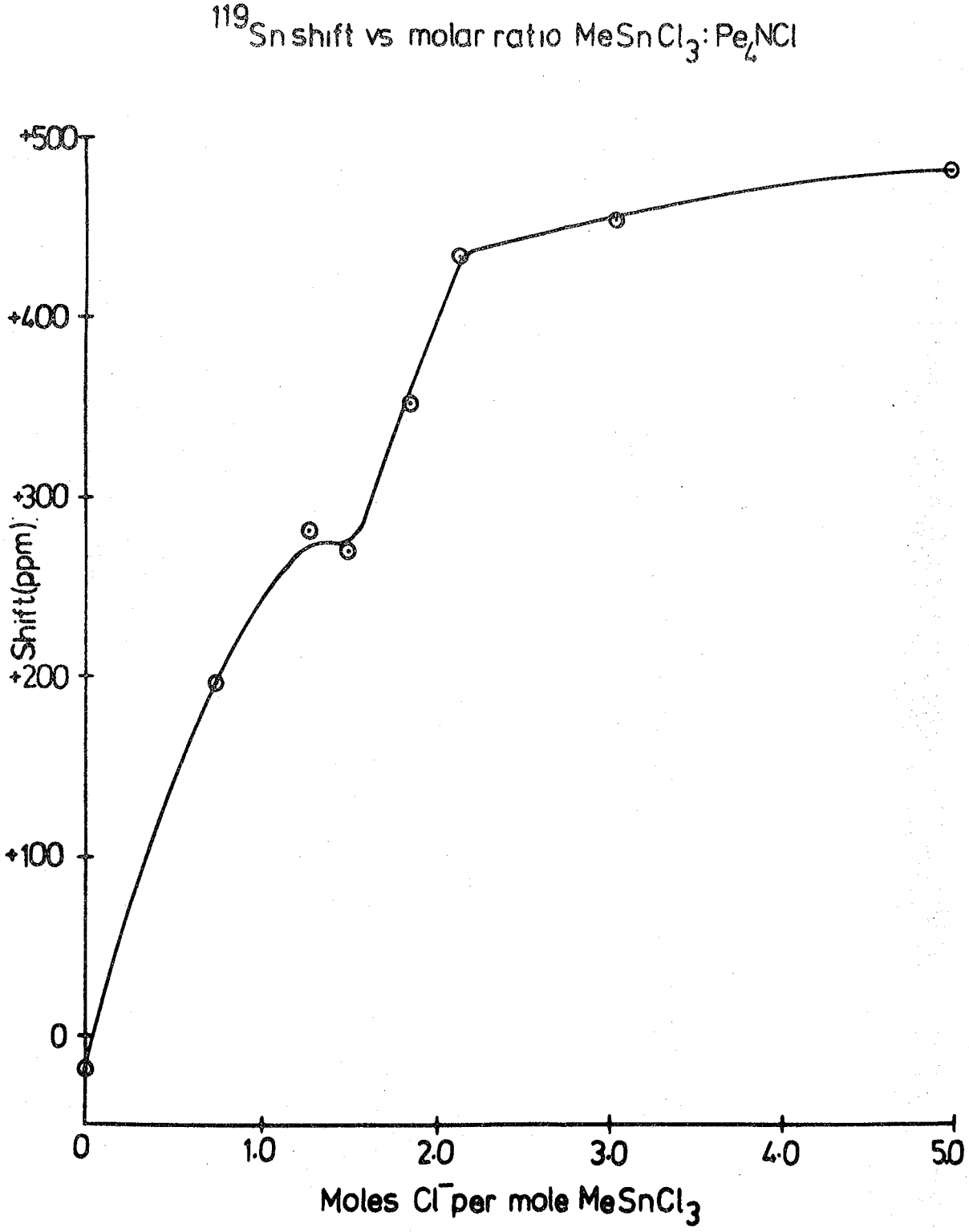
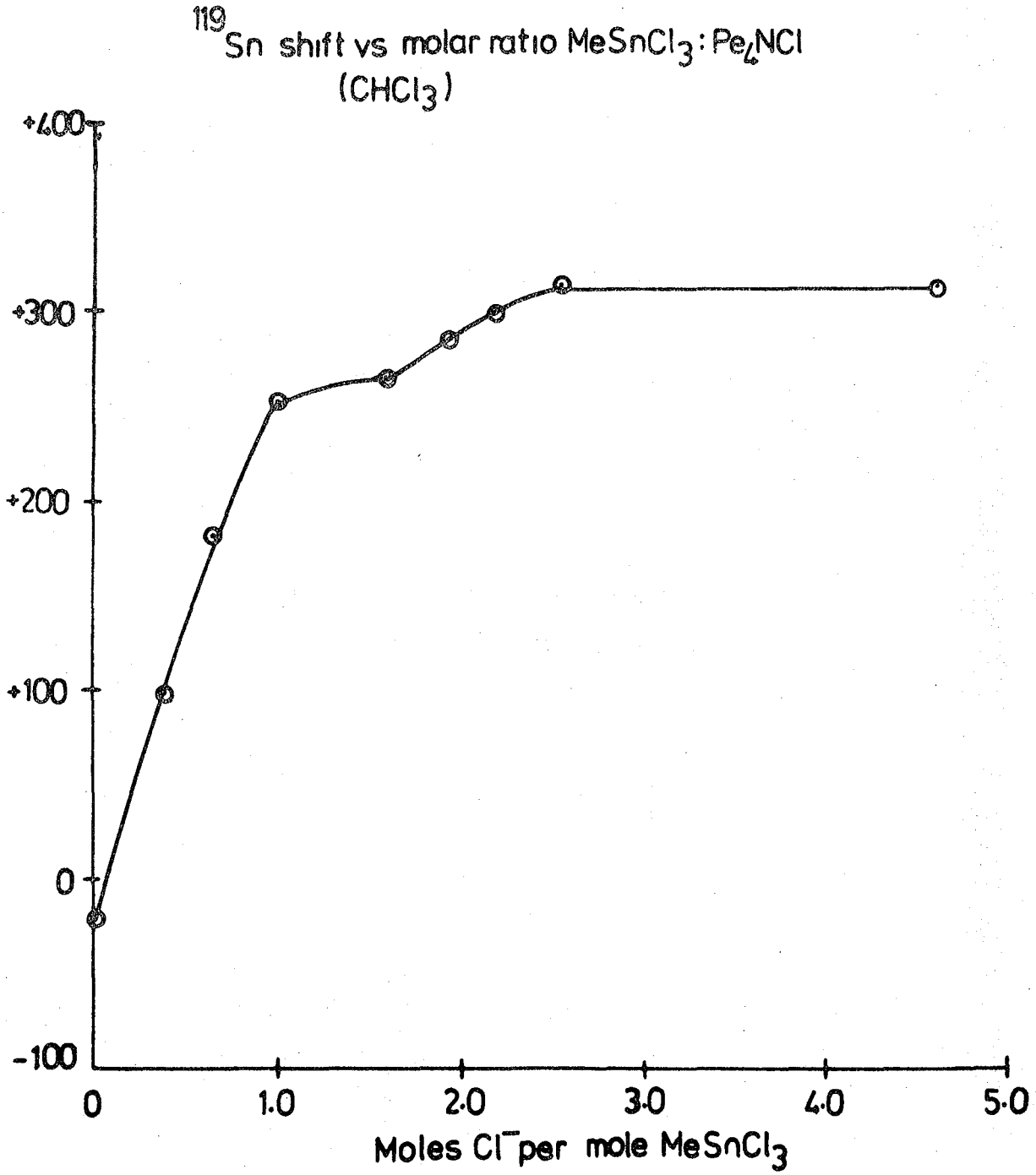

^{119}Sn shift vs molar ratio $MeSnCl_3$: Pe_4NCl
+500
+400
+300
+200
+100
0
Shift(ppm)
0
1.0
2.0
3.0
4.0
5.0
Moles Cl^- per mole $MeSnCl_3$

Fig. 5


119Sn shift vs molar ratio MeSnCl3 : Pe4NCl
(CHCl3)
+400
+300
+200
+100
0
-100
0
1.0
2.0
3.0
4.0
5.0
Moles Cl⁻ per mole MeSnCl3

Cl^- ions, ultimately forming the 6-coordinate complex $[MeSnCl_5]^{2-}$ via the intermediate, 5-coordinate complex, $[MeSnCl_4]^-$. A surprising feature is the large chemical shift difference at high chloride concentration between the two solvent systems, despite the similarity in the shifts of the 5-coordinate intermediates. It would appear that a true 'end-point' is reached in chloroform at + 314.2 ppm, and this is assumed to be the shift of the isolated 6-coordinate anion. The curve for the methylene chloride system does not level off, however, but continues rising to higher chemical shifts, suggesting that some form of ion-association such as ion-pair formation, is taking place in this solvent. A similar feature was observed in the graph for diphenyltindichloride reacting with tetrapentylammonium chloride in CH_2Cl_2 solvent. This is despite the fact that methylene chloride has a slightly lower dielectric constant than chloroform, which on this basis alone would make it the poorer of the two solvents for ion-aggregation. The alternative postulate of addition of further Cl^- to the six-coordinate species appears highly improbable. ^{119}Sn n.m.r. shifts are clearly very sensitive to environment, as shown by the large range of solvent effects on tin(IV) species,[22] so that increased aggregation could cause an increase in shielding, and hence an upfield shift. Unfortunately the complex formation between $MeSnCl_3$ and Et_4NCl, where ion-pair formation would be less likely to occur, could not be followed by ^{119}Sn n.m.r. because of solubility problems.

The white solid product isolated from reaction of a 1:2 ratio of $MeSnCl_3$ and Et_4NCl in methylene chloride had an infra-red spectrum (Appendix 1, no. 3) which closely resembled that reported in the literature[31] for $(Et_4N)_2[MeSnCl_5]$. The Raman spectrum of the product (Appendix 2, no. 3) also differed from that expected from a combination of starting materials.

(iv) Ph_3SnCl + Et_4NCl

The variation of ^{119}Sn chemical shift with addition of Et_4NCl was monitored in methylene chloride solvent. The results obtained are listed in Table 11.

TABLE 11 Chemical Shift Variation for the Ph_3SnCl/Cl^- System

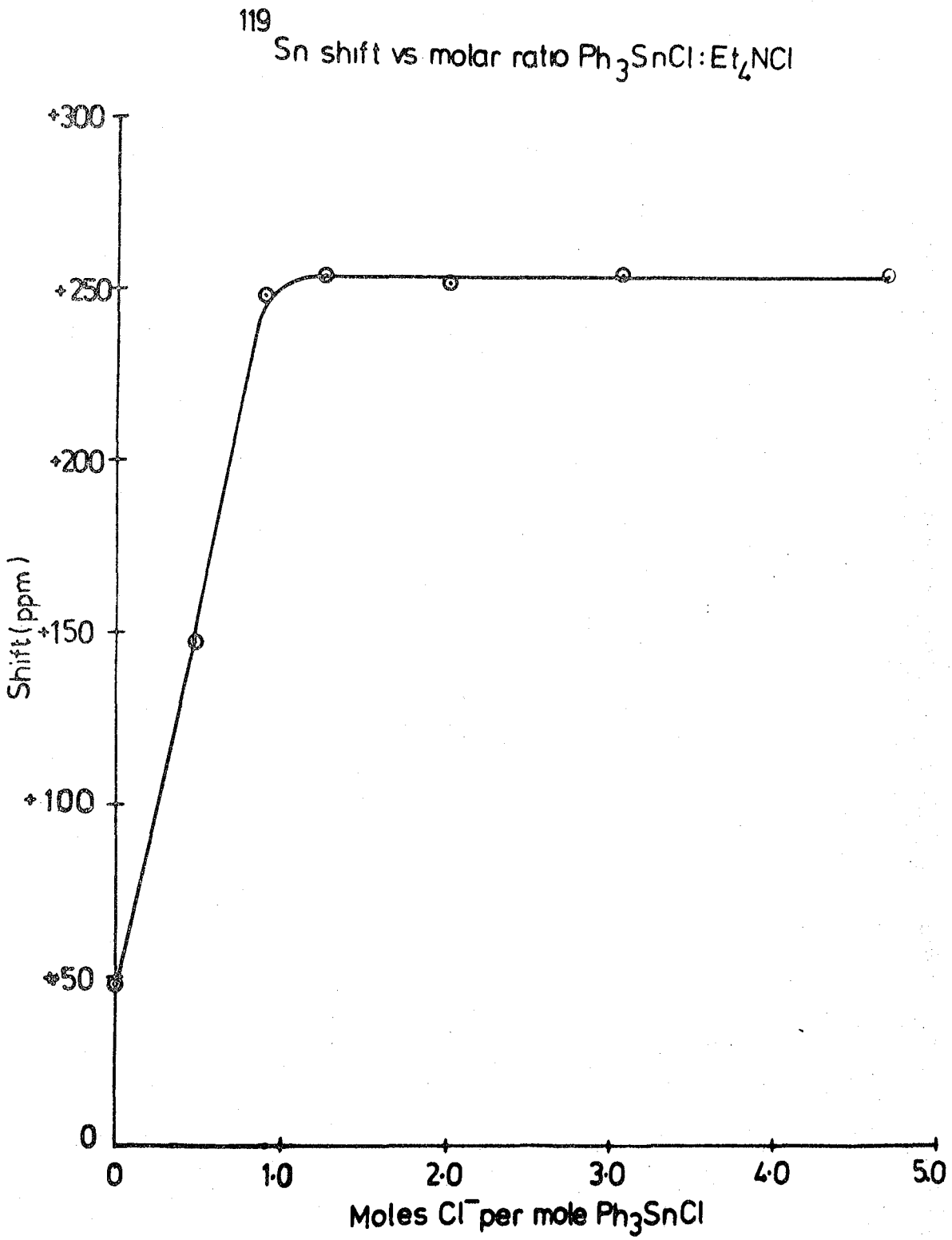
Molar Ratio $Ph_3SnCl:Et_4NCl$	^{119}Sn Chemical Shift (ppm)
1:0.00	+ 48.0
1:0.47	+ 146.6
1:0.89	+ 247.9
1:1.25	+ 253.7
1:2.00	+ 252.1
1:3.05	+ 254.8
1:4.67	+ 254.8

When these results were plotted on a graph (Fig. 6), a single-stage curve was obtained , suggesting a one-step reaction, and the addition of only one Cl^- ion, forming the 5-coordinate anionic complex, $[Ph_3SnCl_2]^-$.

The white solid product isolated from reaction of a 1:1 molar ratio of starting materials gave an infra-red spectrum (Appendix 1, no. 4) in good agreement with that reported in the literature[3] for $(Et_4N)[Ph_3SnCl_2]$. The Raman spectrum of the product (Appendix 2, no. 4) also differed from that expected from a combination of starting materials.

The ^{119}Sn n.m.r. spectrum of the product in methylene chloride

Fig. 6


119
Sn shift vs molar ratio $Ph_3SnCl:Et_4NCl$
+300
+250
+200
+150
+100
+50
0
Shift (ppm)
0
1·0
2·0
3·0
4·0
5·0
Moles Cl^- per mole Ph_3SnCl

yielded a single peak at + 247.9 ppm, very close to the limiting shift reported in the above experiment. This suggests that very little dissociation of $[Ph_3SnCl_2]^-$ occurs in solution.

(v) Ph_2SnCl_2 + Pe_4NCl

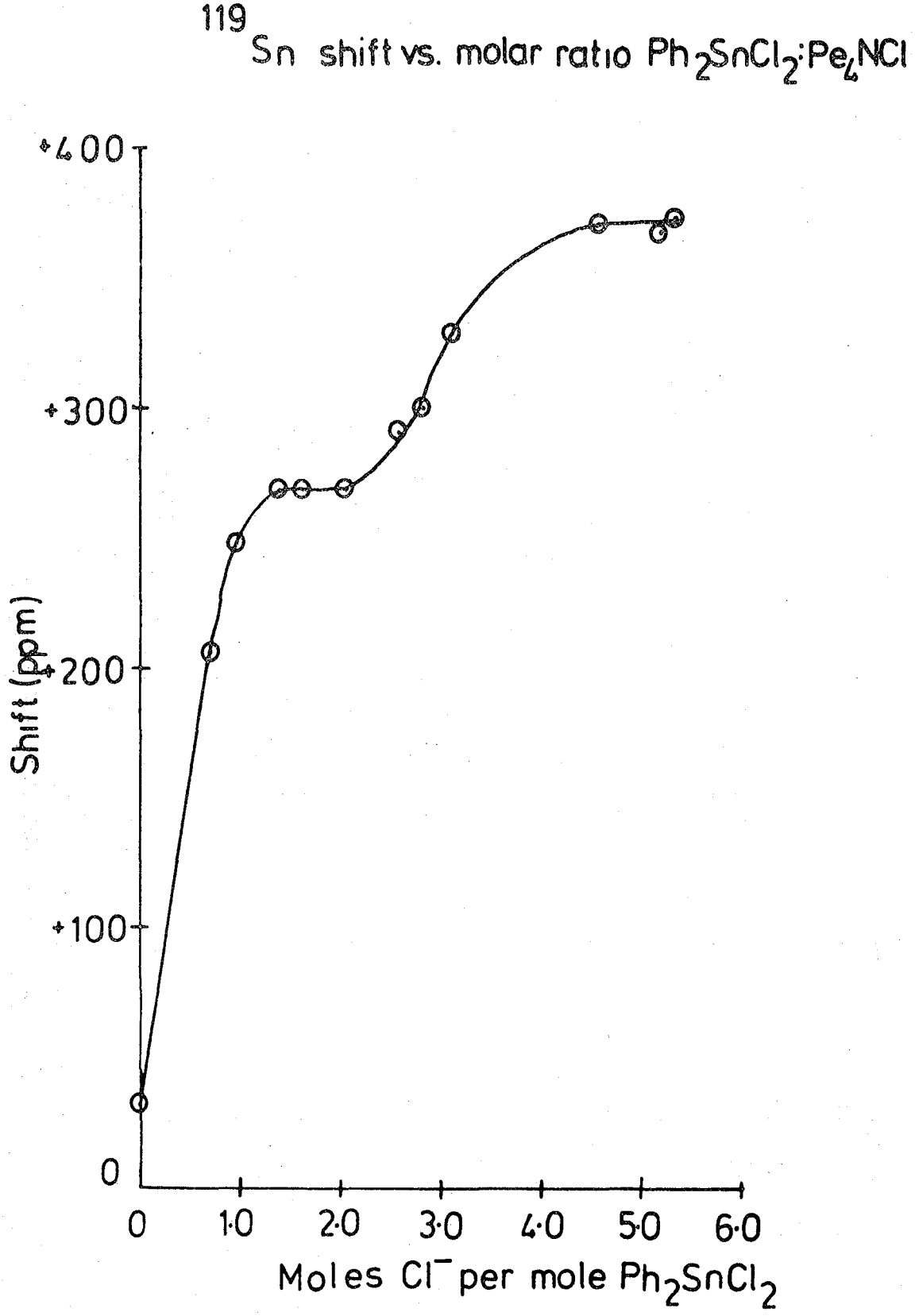
The variation of ^{119}Sn chemical shift with addition of Pe_4NCl was monitored in CH_2Cl_2 solvent. The results obtained are listed in Table 12.

TABLE 12 Chemical Shift Variation for the Ph_2SnCl_2/Cl^- System

Molar Ratio Ph_2SnCl_2:Pe_4NCl	^{119}Sn Chemical Shift (ppm)
1:0.00	+ 32.0
1:0.71	+ 206.0
1:0.95	+ 247.9
1:1.38	+ 268.8
1:1.61	+ 268.8
1:2.11	+ 268.9
1:2.56	+ 291.5
1:2.83	+ 300.2
1:3.11	+ 328.3
1:4.55	+ 370.2
1:5.17	+ 366.9
1:5.30	+ 373.7

When these results were plotted on a graph (Fig. 7), a 2-stage curve was obtained, suggesting a two-step reaction, involving the addition of

Fig. 7


119Sn shift vs. molar ratio Ph2SnCl2:Pe4NCl
+400
+300
+200
+100
0
Shift (ppm)
0
1·0
2·0
3·0
4·0
5·0
6·0
Moles Cl⁻ per mole Ph2SnCl2

2 Cl^- ions to form the six-coordinate di-anion, $[Ph_2SnCl_4]^{2-}$ via the intermediate, 5-coordinate anion, $[Ph_2SnCl_3]^-$.

The white solid product isolated from reaction of a 1:2 molar ratio of starting materials had an infra-red spectrum (Appendix 1, no. 5) which clearly differed from that expected from a combination of starting material spectra. The Raman spectrum of the product (Appendix 2, no.4) was also different from the combined spectra of starting materials, showing that adduct formation had taken place.

The ^{119}Sn n.m.r. spectrum of the product in methylene chloride solvent yielded a single shift at + 268.9 ppm. This is identical to the shift of the 5-coordinate anionic complex, $[Ph_2SnCl_3]^-$ as obtained from the graph, indicating that dissociation of the six-coordinate complex in a non-polar solvent is extensive.

(vi) $PhSnCl_3$ + Pr_4NCl

The variation of ^{119}Sn chemical shift with addition of Pr_4NCl was monitored in methylene chloride solvent. The results obtained are listed in Table 13.

When these results were plotted on a graph (Fig. 8) a 2-stage curve was obtained, suggesting the stepwise addition of two Cl^- ions, going via the 5-coordinate complex $[PhSnCl_4]^-$, to the 6-coordinate complex $[PhSnCl_5]^{2-}$.

The white solid isolated from reaction of a 1:2 molar ratio of $PhSnCl_3$ and Pr_4NCl had an infra-red spectrum (Appendix 1, no.6) which clearly differed from the combined spectra of starting materials. The Raman spectrum of the product (Appendix 2, no. 6) also differed from that expected from a combination of starting materials.

In methylene chloride solvent, the ^{119}Sn n.m.r. spectrum of the

Fig. 8

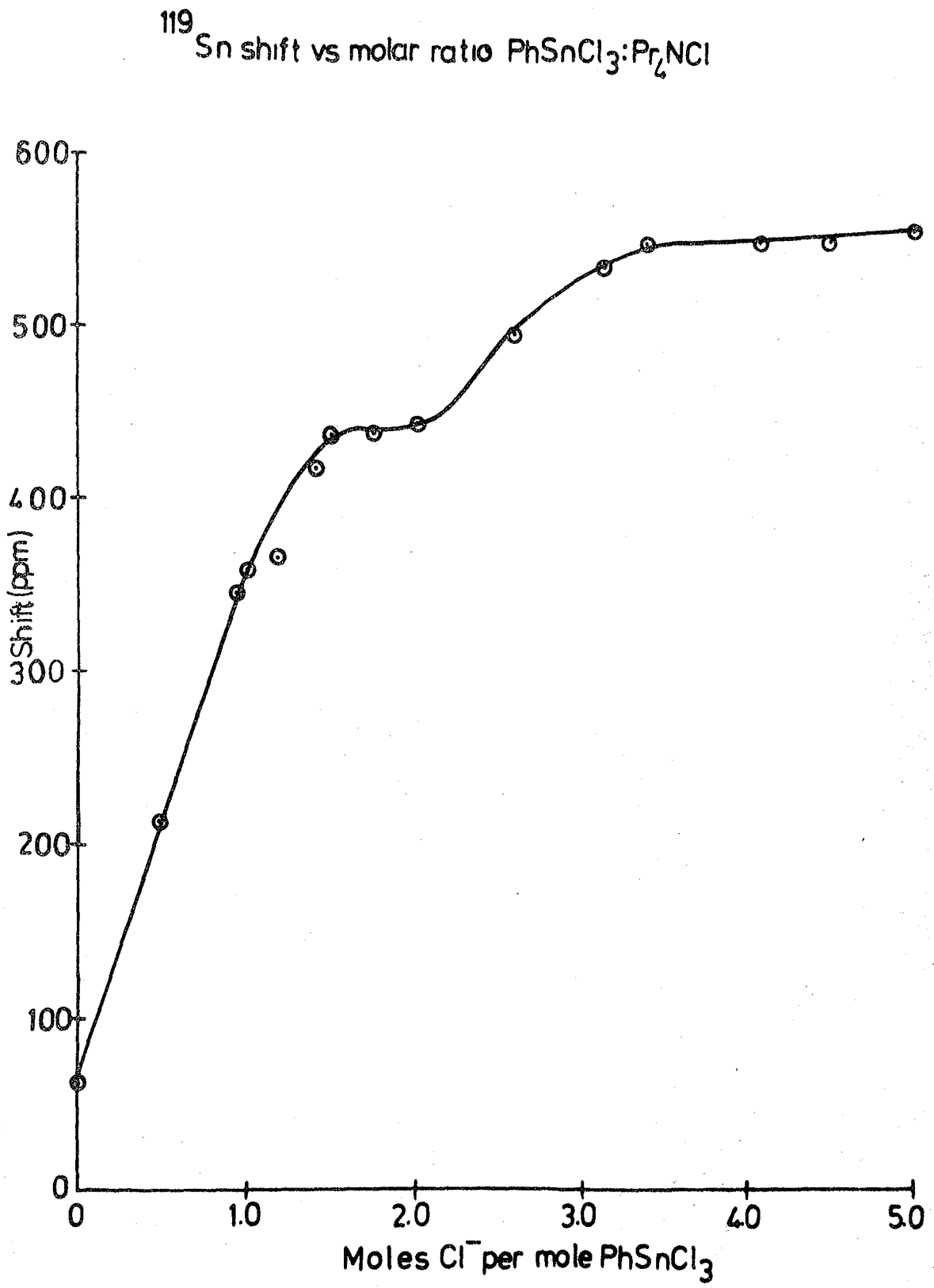

119Sn shift vs molar ratio PhSnCl3:Pr4NCl
600
500
400
300
200
100
0
δ Shift (ppm)
0
1.0
2.0
3.0
4.0
5.0
Moles Cl⁻ per mole PhSnCl3

TABLE 13 Chemical Shift Variation for the $PhSnCl_3/Pr_4NCl$ System

Molar Ratio $PhSnCl_3:Pr_4NCl$	^{119}Sn Chemical Shift (ppm)
1:0.00	+ 63.0
1:0.49	+ 216.5
1:0.93	+ 345.7
1:1.00	+ 359.8
1:1.18	+ 364.7
1:1.41	+ 417.5
1:1.49	+ 436.6
1:1.77	+ 433.7
1:2.00	+ 437.3
1:2.57	+ 495.5
1:3.12	+ 530.8
1:3.43	+ 547.2
1:4.07	+ 547.9
1:4.47	+ 547.9
1:5.00	+ 554.1

product yielded a single peak at + 541.1 ppm, suggesting only a very small degree of dissociation on $[PhSnCl_5]^{2-}$ in solution.

(vii) $R_4Sn + Et_4NCl$

Although under normal circumstances, neither tetramethyl- not tetraphenyltin show any acceptor properties, the reactions with chloride ion were carried out for completeness.

(a) Me_4Sn

Reaction was carried out between a 1:2 molar ratio of Me_4Sn and Et_4NCl in methylene chloride. The white solid product isolated had an infra-red spectrum (Appendix 1, no. 7) corresponding to that of Et_4NCl (Appendix 1, no. 8). This was also the case with the Raman spectrum (Appendix 2, no. 7), proving that only starting materials had been regenerated (the Me_4Sn had obviously been pumped off under vacuum with the solvent). To ascertain whether adduct formation occurred in solution, two n.m.r. tubes were prepared containing different molar ratios of Me_4Sn and Et_4NCl in methylene chloride solvent. The ^{119}Sn n.m.r. spectra were then run and the results obtained are listed in Table 14.

TABLE 14 ^{119}Sn N.m.r. Shifts of Me_4Sn on Addition of Cl^- Ion

Molar Ratio $Me_4Sn:Et_4NCl$	^{119}Sn Shift on same day	^{119}Sn Shift after 1 week
1:0.96	- 1.7 ppm	+ 0.0 ppm
1:2.36	- 5.1 ppm	+ 2.5 ppm

These shifts are all close to the value for Me_4Sn (0.0 ppm) indicating that the only Sn-containing species in solution is Me_4Sn and that no adduct-formation occurs.

(b) Ph_4Sn

Reaction was carried out between a 1:2 molar ratio of Ph_4Sn and Et_4NCl in methylene chloride solvent. The white solid product isolated had an infra-red spectrum (Appendix 1, no. 9) corresponding to the

combined spectra of Ph_4Sn (Appendix 1, no. 10) and Et_4NCl. This was also the case with the Raman spectra (Appendix 2, no. 8), proving that adduct formation had not taken place.

Because of the low solubility of Ph_4Sn in non-polar solvents, n.m.r. solution studies on possible products were not attempted.

(viii) Ph_3SnBr + Pr_4NBr

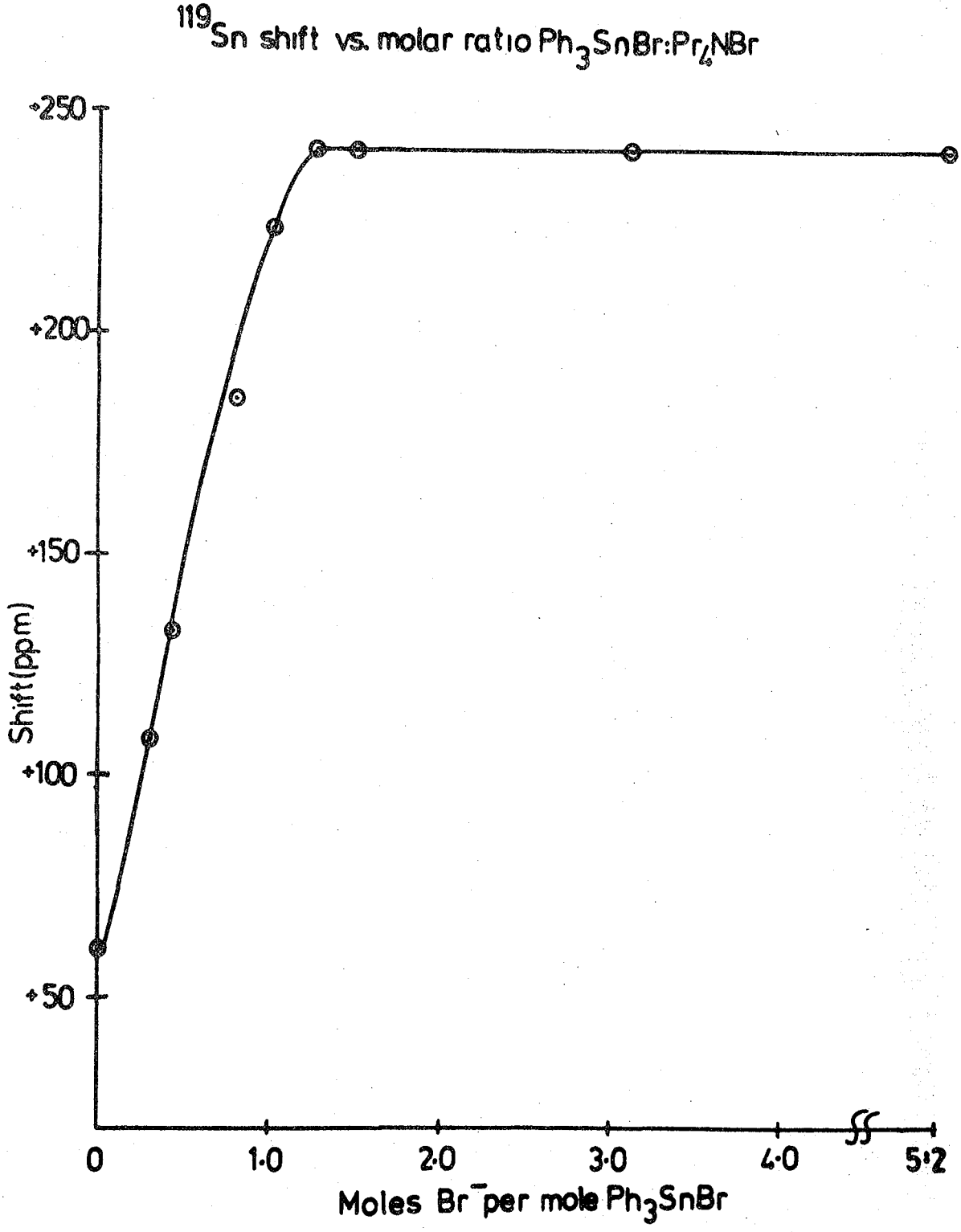
The variation of ^{119}Sn chemical shift with addition of Pr_4NBr was monitored in methylene chloride solvent. The results obtained are listed in Table 15.

TABLE 15 Chemical Shift Variation for the Ph_3SnBr/Pr_4NBr System

Molar Ratio $Ph_3SnBr:Pr_4NBr$	^{119}Sn Chemical Shift (ppm)
1:0.00	+ 60.5
1:0.29	+ 108.2
1:0.42	+ 132.7
1:0.79	+ 185.0
1:1.00	+ 223.4
1:1.25	+ 240.9
1:1.48	+ 240.9
1:3.10	+ 240.9
1:5.23	+ 240.9

When these results were plotted on a graph (Fig. 9), a single stage curve was obtained, indicating the addition of one Br^- ion to

Fig. 9


^{119}Sn shift vs. molar ratio $Ph_3SnBr:Pr_4NBr$
+250
+200
+150
+100
+50
Shift (ppm)
0
1·0
2·0
3·0
4·0
5·2
Moles Br^- per mole Ph_3SnBr

form the 5-coordinate complex anion, $[Ph_3SnBr_2]^-$.

The white solid isolated from reaction of a 1:1 molar ratio of starting materials had an infra-red spectrum (Appendix 1, no. 11) which differed from that expected from a combination of starting materials, although no literature spectrum could be found for comparison. The Raman spectrum of the product (Appendix 2, no. 9) also differed from that expected from a combination of starting materials.

The ^{119}Sn n.m.r. spectrum of the product in methylene chloride yielded a single peak at + 237.6 ppm. This is very close to the limiting shift, suggesting that dissociation of $[Ph_3SnBr_2]^-$ in solution is negligible.

(ix) Me_3SnBr + Pr_4NBr

The variation of ^{119}Sn chemical shift with addition of Pr_4NBr was monitored in methylene chloride solvent. The results obtained are listed in Table 16.

TABLE 16 Chemical Shift Variation for the Me_3SnBr/Pr_4NBr System

Molar Ratio $Me_3SnBr:Pr_4NBr$	^{119}Sn Chemical Shift (ppm)
1:0.00	- 130.7
1:0.77	- 14.0
1:1.34	+ 29.0
1:2.39	+ 43.0
1:2.69	+ 40.2
1:4.00	+ 44.2
1:4.30	+ 41.9
1:5.40	+ 45.4

When these results were plotted on a graph (Fig. 10), a one-stage curve was obtained, suggesting the addition of one Br^- ion to form the 5-coordinate complex, $[Me_3SnBr_2]^-$. Due to lack of starting material, isolation and characterisation of the solid adduct was not attempted.

(x) Me_2SnBr_2 + Bu_4NBr

The variation of ^{119}Sn chemical shift with addition of Bu_4NBr was monitored in methylene chloride solvent. The results obtained are listed in Table 17.

TABLE 17 Chemical Shift Variation for the Me_2SnBr_2/Bu_4NBr System

Molar ratio Me_2SnBr_2:Bu_4NBr	^{119}Sn Chemical Shift (ppm)
1:0.00	- 74.5
1:0.34	+ 8.1
1:0.58	+ 64.0
1:1.00	+ 152.5
1:1.17	+ 154.8
1:1.42	+ 159.4
1:2.02	+ 164.1
1:2.31	+ 165.2
1:2.81	+ 174.6
1:3.52	+ 181.5
1:6.01	+ 180.4

When these results were plotted on a graph (Fig. 11), a 2-stage curve was obtained, although the change in chemical shift between the

Fig. 10

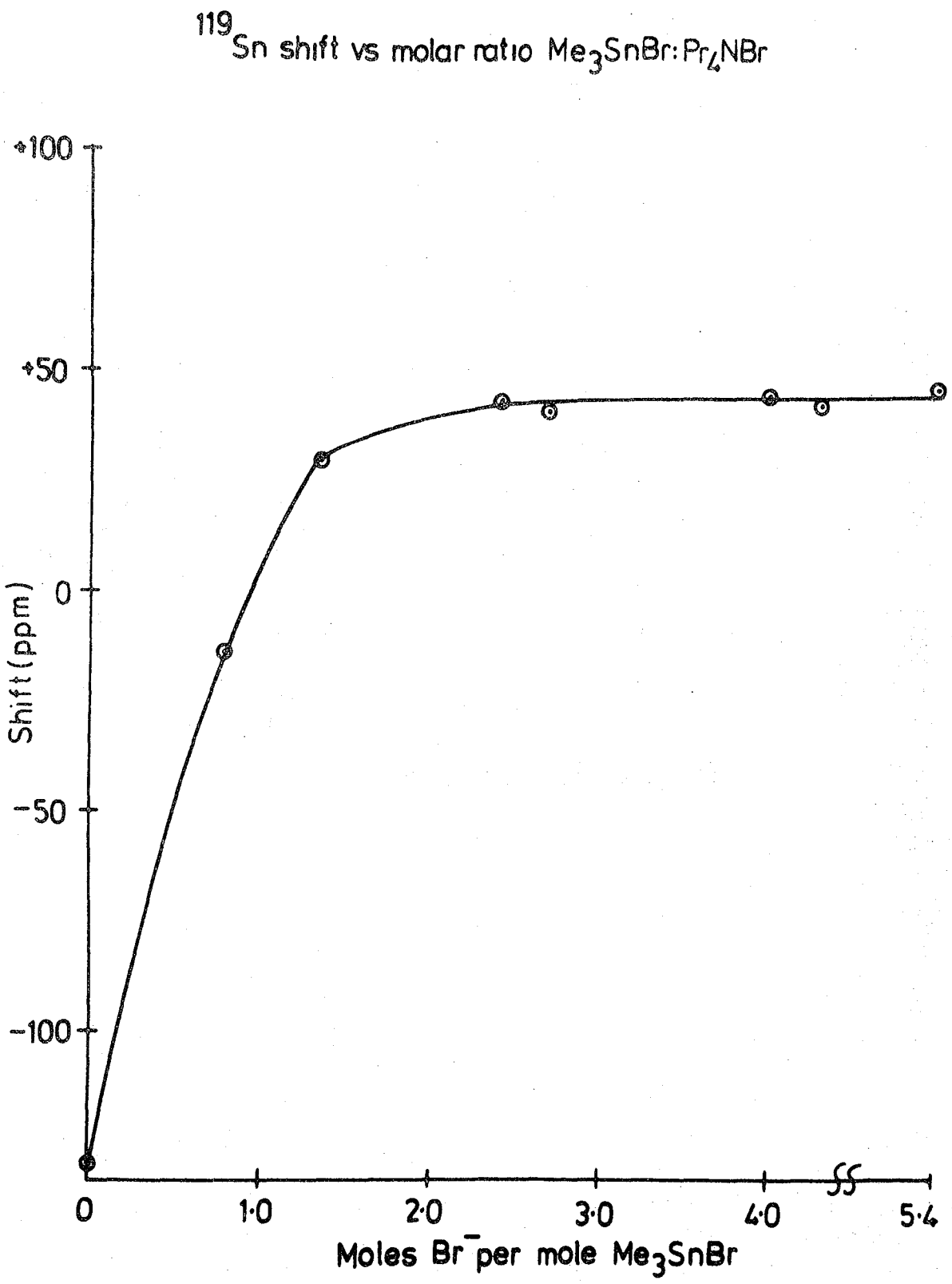
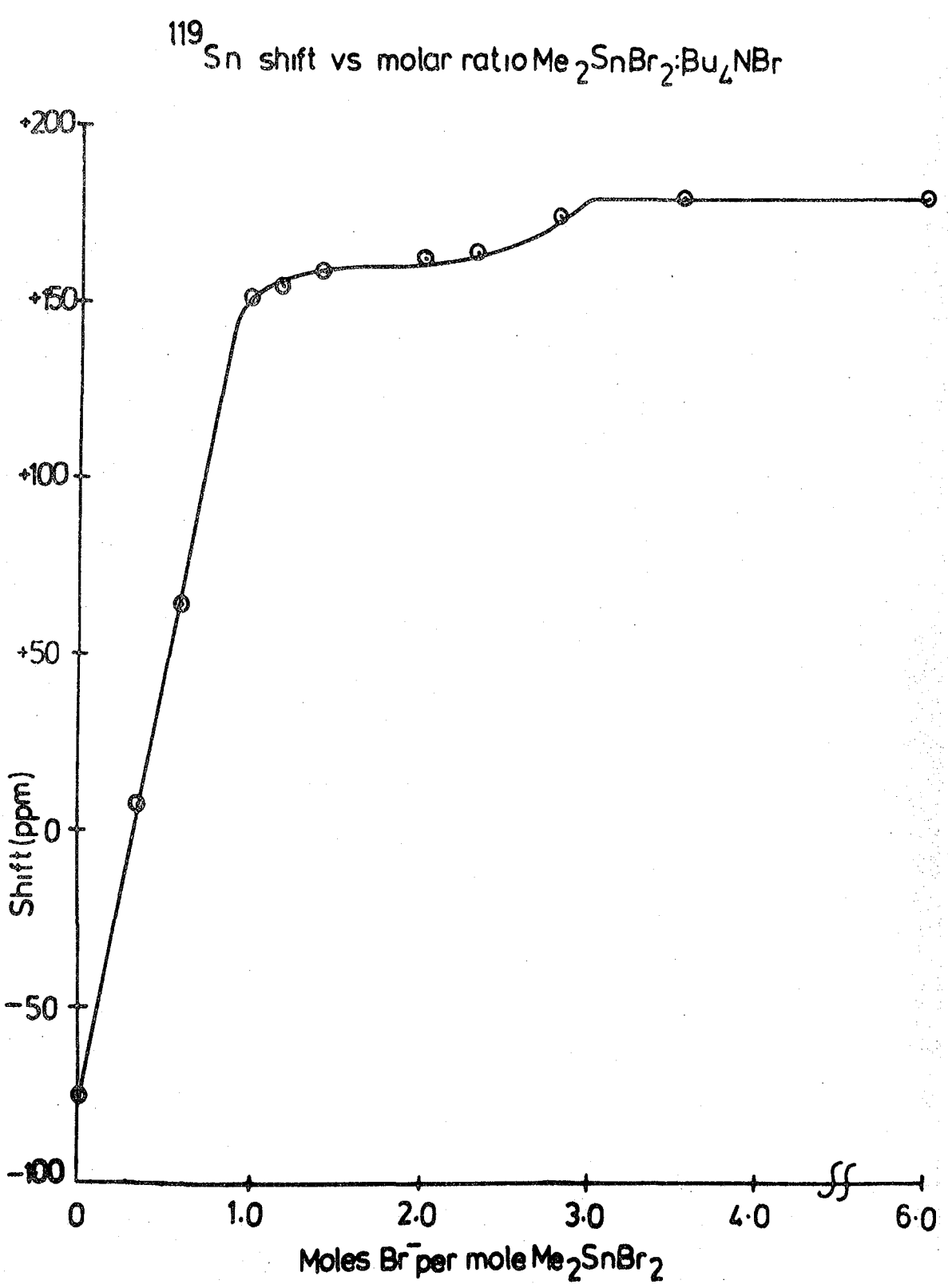

^{119}Sn shift vs molar ratio $Me_3SnBr:Pr_4NBr$
+100
+50
0
-50
-100
Shift (ppm)
0
1·0
2·0
3·0
4·0
5·4
Moles Br^- per mole Me_3SnBr

Fig. 11


119Sn shift vs molar ratio Me2SnBr2:Bu4NBr
+200
+150
+100
+50
0
-50
-100
Shift (ppm)
0
1.0
2.0
3.0
4.0
6.0
Moles Br⁻ per mole Me2SnBr2

two stages was relatively small. By analogy with the dimethyltin dichloride/Cl^- system, a 2-step addition process might be expected, but this is certainly not clear-cut from the graph. Raman spectroscopy was therefore used to confirm whether the main Sn-containing species isolated from a 1:2 mixture of Me_2SnBr_2 and Bu_4NBr was the 1:1 adduct or the 1:2 adduct. The data obtained are listed in Table 18.

TABLE 18 Raman Data for the Me_2SnBr_2/Bu_4NBr System

System	Spectrum (150 - 650 cm^{-1})
Bu_4NBr	264 (vw)
Me_2SnBr_2	222 (vs), 230 (sh), 515 (vs), 567 (w)
Me_2SnBr_2+ Bu_4NBr (1:1)	230 (m), 514 (s), 559 (vw).
Me_2SnBr_2 + Bu_4NBr (1:2)	515 (w)

The Raman data suggest that the product isolated from reaction of both 1:1 and 1:2 molar ratios is $(Bu_4N)_2[Me_2SnBr_4]$, since the spectrum of the product from a 1:2 molar ratio is virtually featureless below 1000 cm^{-1}, whereas that of the product from a 1:1 molar ratio clearly shows the presence of unreacted Me_2SnBr_2 , which is consistent with:

(a) $Me_2SnBr_2 + 2Bu_4NBr \longrightarrow (Bu_4N)_2[Me_2SnBr_4]$ 3(1)

(b) $2Me_2SnBr_2 + 2Bu_4NBr \longrightarrow (Bu_4N)_2[Me_2SnBr_4] + Me_2SnBr_2$ 3(2)

Infra-red spectroscopy was of little use in this case due to a

lack of strong bands below 700 cm^{-1} in the products.

The ^{119}Sn n.m.r. spectrum of the product isolated from reaction of a 1:2 ratio of starting materials yielded a single peak at + 160.1 ppm in methylene chloride. This is lower than the limiting shift of the proposed 6-coordinate adduct, and it therefore appears that dissociation to the 5-coordinate adduct occurs to a considerable extent in solution.

B. Study of Mixed Halogen Adducts by ^{119}Sn N.m.r.

Products were isolated from the reaction of an organotin(IV) chloride with a Br^- donor, and vice versa. The reciprocal products were investigated by ^{119}Sn n.m.r. as well as conventional techniques, in an attempt to establish whether the same Sn-containing product had formed in each case.

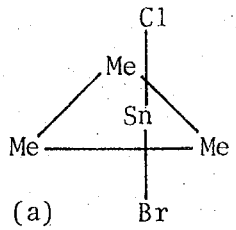
(i) Me_3SnCl/Bu_4NBr and Me_3SnBr/Et_4NCl

The product isolated from the reaction of a 1:1 molar ratio of Me_3SnCl and Bu_4NBr was a white powder, whereas that isolated from reaction of Me_3SnBr with Et_4NCl was pale yellow in colour. The data obtained for the two products are listed in Table 19.

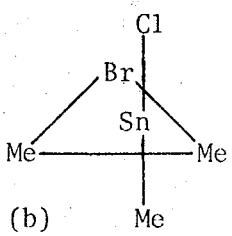
TABLE 19 Comparison of Spectroscopic Data for the Systems Me_3SnCl/Br^- and Me_3SnBr/Cl^-

	^{119}Sn n.m.r. shift in CH_2Cl_2	Infra-red(cm^{-1}) (< 650 cm^{-1})	Raman (cm^{-1}) (150-650 cm^{-1})
Me_3SnCl/Br^-	+ 26.0 ppm	546	510, 547
Me_3SnBr/Cl^-	+ 9.7 ppm	540	509, 544

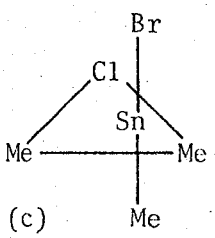
From infra-red (Appendix 1, nos. 12, 13) and Raman data alone, it appears that the same anionic complex had formed in both cases. The ^{119}Sn n.m.r. shifts are somewhat different, however, which suggests that different isomers could have formed in the two reactions. There are 4 possible isomers for a 5-coordinate, trigonal bipyramidal anion (see below) but of these structure (a), with both electronegative groups



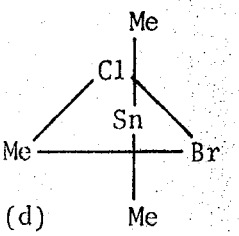
Cl axial
Br axial



Cl axial
Br equat.



Br axial
Cl equat.



Cl equat.
Br equat.

axial, is the most probable. The more electronegative group is Cl, which is reasonably certain to prefer the axial position, but structure (b) could also be possible, with the bromine occupying an equatorial position. Formation of these two isomers in the two reactions could account for the difference in ^{119}Sn n.m.r. shifts. Alternatively, the difference in shifts could simply be due to slightly more dissociation in the system with the lower shift.

(ii) Me_2SnCl_2/Bu_4NBr and Me_2SnBr_2/Et_4NCl

Both products isolated from the reaction of a 1:2 molar ratio of organotin halide and halide donor were amorphous white solids, and the data obtained from investigation by spectroscopic techniques are listed in Table 20.

TABLE 20 Spectroscopic Data for the Systems $Me_2SnCl_2/2Br^-$ and $Me_2SnBr_2/2Cl^-$

	^{119}Sn Chemical Shift (ppm)[a]	Infra-red (650-250 cm^{-1})[b]	Raman (150-650 cm^{-1})
Me_2SnBr_2 + $2Cl^-$	+ 136.2	325, 511, 559	327(w), 502(vw,sh), 514(vs), 564(w).
Me_2SnCl_2 + $2Br^-$	+ 137.3	570	189(m), 393(w), 508(vs).

a In CH_2Cl_2 solvent. b Appendix 1, nos. 14, 15.

Obviously the same anionic complex has formed in both cases, since the ^{119}Sn chemical shifts are almost identical. Various isomers are again possible, but the results indicate that one of these must be formed preferentially.

The bands at $\sim$ 510 cm^{-1} in the Raman spectra probably arise from the anion and the observation that there are no obvious coincidences in the i.r. spectra is probably an indication that the anion bands are either i.r. inactive or are too weak to be observed in the spectra recorded.

3. Summary

From the results obtained, it was found that in a non-polar solvent, the following addition reactions take place between organotin chlorides (or bromides) and the appropriate halide donor:

$$R_3SnX + X^- \longrightarrow R_3SnX_2^- \xrightarrow{X^-} \text{no reaction} \qquad 3(3)$$

$$R_2SnX_2 + X^- \longrightarrow R_2SnX_3^- \xrightarrow{X^-} R_2SnX_4^{2-} \qquad 3(4)$$

$$RSnX_3 + X^- \longrightarrow RSnX_4^- \xrightarrow{X^-} RSnX_5^{2-} \qquad 3(5)$$

(R = Me, Ph; X = Cl, Br)

A summary of the ^{119}Sn n.m.r. solution shifts for proposed 5- and 6-coordinate complexes (and the appropriate molar ratios at which each is dominant), as well as the shifts of isolated products in non-polar solvents is given in Table 21.

The following addition reactions were also found to occur on reaction of organotin chlorides with Br^- donors, and vice versa:

$$\text{(a)}\quad Me_3SnCl + Bu_4NBr \longrightarrow (Bu_4N)[Me_3SnClBr] \qquad 3(6)$$

$$\text{(b)}\quad Me_3SnBr + Et_4NCl \longrightarrow (Et_4N)[Me_3SnBrCl] \qquad 3(7)$$

$$\text{(c)}\quad Me_2SnCl_2 + 2Bu_4NBr \longrightarrow (Bu_4N)_2[Me_2SnCl_2Br_2] \qquad 3(8)$$

$$\text{(d)}\quad Me_2SnBr_2 + 2Et_4NCl \longrightarrow (Et_4N)_2[Me_2SnBr_2Cl_2] \qquad 3(9)$$

^{119}Sn n.m.r. spectroscopy suggests that in both (a) or (b), and (c) or (d), the same anionic complex may be formed.

4. Experimental

The approach used in the preparation and isolation of these complexes was as follows. Starting materials were weighed to the correct stoichiometric ratios outside the glove-box in stoppered sample bottles, all adjustments to the weight being made inside the box due to the moisture-sensitivity of most of the starting materials. Both reactants were

TABLE 21 Summary of Chemical Shift[a] Data Obtained from Halide Addition Experiments

	In Solution				After Product Isolation	
System	^{119}Sn shift[b] of 5-coordinate complex (ppm)	Limits of optimum molar ratios	^{119}Sn shift[b] of 6-coordinate complex (ppm)	Minimum molar ratio	Proposed product	^{119}Sn shift (ppm)
Me_3SnCl + Et_4NCl	+ 61.1	> 1:2.0	-	-	$(Et_4N)(Me_3SnCl_2)$	+ 47.7
Me_2SnCl_2 + Et_4NCl	+ 126.8	1:1.3 to 1:2.0	+ 166.5	1:2.9	$(Et_4N)_2(Me_2SnCl_4)$	+ 128.0
$MeSnCl_3$ + Pe_4NCl ($CHCl_3$)	+ 258.6	1:1.1 to 1:2.0	+ 314.2	1:2.5	$(Et_4N)_2(MeSnCl_5)$	
$MeSnCl_3$ + Pe_4NCl	+ 274.1	1:1.3 to 1:1.5	~ + 467.8	~ 1:3.0[c]		
Ph_3SnCl + Et_4NCl	+ 253.9	> 1:1.2	-	-	$(Et_4N)(Ph_3SnCl_2)$	+ 247.9
Ph_2SnCl_2 + Pe_4NCl	+ 268.8	1.13 to 1.21	+ 370.3	> 1:4.2	$(Pe_4N)_2(Ph_2SnCl_4)$	+ 268.9
$PhSnCl_3$ + Pr_4NCl	+ 435.9	1:1.5 to 1:2.0	+ 549.3	> 1:3.3	$(Pe_4N)_2(PhSnCl_5)$	+ 541.1

TABLE 21 (Continued)

	In Solution				After Product Isolation	
System	^{119}Sn shift[b] of 5-coordinate complex (ppm)	Limits of optimum molar ratios	^{119}Sn shift[b] of 6-coordinate complex (ppm)	Minimum molar ratio	Proposed product	^{119}Sn shift (ppm)
Ph_3SnBr + Pr_4NBr	+ 240.9	> 1:1.25	-	-	$(Pr_4N)(Ph_3SnBr_2)$	+ 237.6
Me_3SnBr + Pr_4NBr	+ 42.9	> 1:2.4	-	-	-	-
Me_2SnBr_2 + Bu_4NBr	+ 162.9	1:1.4 to 1:2.2	+ 181.0	> 1:3.0	$(Bu_4N)_2(Me_2SnBr_4)$	+ 160.1

a Unless otherwise stated, all ^{119}Sn chemical shifts were measured in methylene chloride solvent.

b The shift of a 5-coordinate complex is quoted as the mean of all measured shifts falling between the limits of the molar ratios quoted. The shifts of 5-coordinate complexes from the triorganotin halides and all 6-coordinate complexes are quoted as the mean of all measured shifts after the minimum molar ratio.

c Very approximate, since the curve does not level off at a particular molar ratio in this case.

dissolved separately in a minimum amount of a non-polar solvent (usually methylene chloride) after which the two solutions were mixed, and stirred for ∿ 10 minutes to ensure complete reaction. If a sample was required for solution n.m.r., it was withdrawn at this point, otherwise the solution was pumped on the vacuum line to reduce the volume until precipitation occurred. The precipitates were then isolated by filtration, washed well with 30/40 petroleum ether, then dried in vacuo to remove any final traces of solvent. The weights of reactants used, together with analyses, are given in Table 22.

TABLE 22 Experimental Data for the Preparation of Halide Adducts

N.B. The analyst reported a probable loss of tin (in the form of volatile tin halides) during the acid decomposition of many of these compounds making the resulting percentage worthless. Only in cases where this loss of tin was reported as unlikely to have occurred is a tin analysis quoted.

Product	Reactants	g	mmol	Analysis
$(Et_4N)(Me_3SnCl_2)$	Me_3SnCl	1.357	6.80	%found: Cl, 19.5; C, 36.5; H, 8.3; N, 3.3.
	Et_4NCl	1.125	6.80	% requd:Cl, 19.5; C, 36.2; H, 7.9; N, 3.8.
$(Et_4N)_2(Me_2SnCl_4)$	Me_2SnCl_2	0.913	4.15	% found: Cl, 25.7; C, 39.4; H, 9.0; N, 5.3.
	Et_4NCl	1.371	8.30	% requd: Cl, 25.8; C, 39.2; H, 8.3; N, 5.1.
$(Et_4N)_2(MeSnCl_5)$	$MeSnCl_3$	1.094	4.55	% found: Sn, 20.4; Cl, 29.9; C, 35.7; H, 8.5; N, 4.4.
	Et_4NCl	1.511	9.10	% requd: Sn, 20.8; Cl, 31.1; C, 35.7; H, 7.5; N, 4.9.
$(Et_4N)(Ph_3SnCl_2)$	Ph_3SnCl	0.794	2.06	% found: Cl, C, 54.6; H, 7.0; N, 3.0.
	Et_4NCl	0.341	2.06	% requd: Cl, 12.9; C, 56.6; H, 6.4; N, 2.5.
$(Pe_4N)_2(Ph_2SnCl_4)$	Ph_2SnCl_2	0.775	2.25	% found: Sn, 11.5; Cl, 14.8; C, 61.8; H, 10.0; N, 2.3.
	Pe_4NCl	1.503	4.50	% requd: Sn, 11.8; Cl, 14.0; C, 61.7; H, 9.7; N, 2.8.
$(Pe_4N)_2(PhSnCl_5)$	$PhSnCl_3$	1.252	4.14	% found: Sn, 11.4; Cl, 19.3 C, 56.6; H, 9.8; N, 2.5.
	Pe_4NCl	2.761	8.28	% requd: Sn, 12.3; Cl, 18.4; C, 57.2; H, 9.1; N, 2.9.
$(Pr_4N)(Ph_3SnBr_2)$	Ph_3SnBr	0.852	1.98	% found: Sn, 17.2; Br, 23.3 C, 52.4; H, 7.1; N, 2.6.
	Pr_4NBr	0.526	1.98	% requd: Sn, 17.1; Br, 23.0; C, 51.7; H, 6.2; N, 2.0.
$(Bu_4N)_2(Me_2SnBr_2)$	Me_2SnBr_2	0.424	1.37	% found: Br, ; C, 43.5 H, 8.7; N, 3.4.
	Bu_4NBr	0.906	2.81	% requd: Br, 33.6; C, 42.8; H, 8.2; N, 2.9.

TABLE 22 (Continued)

Product	Reactants	g	mmol	Analysis
$(Bu_4N)(Me_3SnClBr)$	Me_3SnCl	0.549	2.75	% found: total halogen, 0.97 ml, 0.1N $AgNO_3$; C, 43.3; H, 8.1; N, 3.7. % requd: total halogen, 0.98 ml, 0.1N $AgNO_3$; C, 43.7; H, 8.6; N, 2.7.
	Bu_4NBr	0.885	2.75	
$(Et_4N)(Me_3SnBrCl)$	Me_3SnBr	0.359	1.47	% found: total halogen, 1.26 ml, 0.1N $AgNO_3$; C, 34.3; H, 6.5; N, 4.6. % requd: total halogen, 1.23 ml, 0.1N $AgNO_3$; C, 32.2; H, 7.1; N, 3.4.
	Et_4NCl	0.249	1.50	
$(Bu_4N)_2$ $(Me_2SnCl_2Br_2)$	Me_2SnCl_2	o.409	1.86	% found: total halogen, 3.63 ml, 0.1N $AgNO_3$; C, 44.2; H, 9.2; N, 2.6. % requd: total halogen, 3.74 ml, 0.1N $AgNO_3$; C, 47.2; H, 9.0; N, 3.2.
	Bu_4NBr	1.202	3.73	
$(Et_4N)_2$ $(Me_2SnBr_2Cl_2)$	Me_2SnBr_2	1.070	3.46	% found: total halogen, 2.30 ml, 0.1N $AgNO_3$; C, 34.2; H, 8.6; N,4.0. % requd: total halogen, 2.20 ml, 0.1N $AgNO_3$; C, 33.8; H, 7.2; N, 4.4.
	Et_4NCl	1.142	6.90	

Chapter 4 REACTIONS WITH LEWIS ACIDS

A. Reactions with Antimony Pentachloride, $SbCl_5$

1. Introduction

The ability of $SbCl_5$ to act as a powerful Lewis acid is well known, and many workers have used this property as a means of forming interesting adducts for structural and other studies.[52,53] By far the most frequent type of reaction undergone by $SbCl_5$ is the formation of adducts by reaction with Lewis bases (electron donors). Many reactions of this type also involve halogen transfer.

$SbCl_5$ is also capable, however, of undergoing exchange reactions with certain organometallic compounds, resulting in the formation of organoantimony(V) chlorides. For example, in 1922, Goddard, Ashley and Evans[54] prepared Ph_2SbCl_3 by reaction of Ph_4Pb with $SbCl_5$. The organoantimony chlorides are all well-known; the compounds R_5Sb, R_4SbCl, and R_3SbCl_2 (where R = Ph, Me) are all stable at ordinary temperatures and have been extensively studied.[12,55-59] The methyl derivatives Me_2SbCl_3 and $MeSbCl_4$ are much less stable than the dichlorides and decompose at or below their melting points by loss of alkylhalide. The aryl derivatives Ph_2SbCl_3 and $PhSbCl_4$, however, are thermally much more stable than Ph_3SbCl_2.

2. Present Work

When this section of the work was embarked upon, it was anticipated that at least some of the reactions attempted would lead to the formation of cationic tin species. This could occur by chloride abstraction from an organotin(IV) chloride, with antimony pentachloride acting as a Lewis acid, as summarized by the following general scheme:

$$R_nSnCl_{4-n} + SbCl_5 \rightarrow R_nSnCl_{3-n}^{+} + SbCl_6^{-} \qquad 4(1)$$

The formation of a cationic, tin-containing species should be readily detectable in solution by ^{119}Sn n.m.r. since a positive charge on the complex would cause substantial deshielding of the Sn-atom, resulting in a large downfield shift of the ^{119}Sn chemical shift relative to the starting material.

It was soon apparent from early results, however, that the reaction postulated above was not taking place. A different reaction was clearly occurring since mixing of starting materials was accompanied by effervescence and evolution of heat, and the resulting solutions yielded ^{119}Sn n.m.r. shifts which differed from those of the starting materials. The reactions of the whole series of phenyltin- and methyltinchlorides with $SbCl_5$ were investigated by ^{119}Sn n.m.r. and conventional techniques. The work may be conveniently subdivided into three sections.

(i) Solution studies of reactions in methylene chloride solvent

Antimony pentachloride, diluted with CH_2Cl_2, was slowly added to a solution of organotin chloride also diluted in CH_2Cl_2, with continuous stirring. In each case, an approximate 1:1 molar ratio was used ($SbCl_5$ being in a slight excess). When the initial vigorous reaction had subsided, a sample of the solution was withdrawn, placed in an n.m.r. tube, and the ^{119}Sn n.m.r. spectrum recorded. The chemical shifts obtained are listed in Table 23, together with ^{119}Sn shifts for the R_nSnCl_{4-n} (R = Me, Ph; n = 0-4) series. If the latter shifts are compared with those obtained in the experiment, it is possible to identify the main tin-containing species formed in solution.

TABLE 23 ^{119}Sn Solution Shifts for Reactions of Organotin Chlorides with $SbCl_5$

Organotin Chloride	^{119}Sn Shift (ppm) in CH_2Cl_2 solvent[a]	^{119}Sn shift (ppm) of solution product from reaction with $SbCl_5$	Main tin-containing species formed
Ph_4Sn	+ 140[b]	+ 29.7	Ph_2SnCl_2
Ph_3SnCl	+ 48	+ 62.9	$PhSnCl_3$
Ph_2SnCl_2	+ 32	+ 62.8, + 162.3[d]	$PhSnCl_3$, $SnCl_4$
$PhSnCl_3$	+ 63	+ 150.1	$SnCl_4$
$SnCl_4$	+ 150	+ 150.1	no reaction
Me_4Sn	0	- 131.7, - 171.3	Me_3SnCl, Me_2SnCl_2
Me_3SnCl	- 155 to -169	- 146.1	Me_2SnCl_2
Me_2SnCl_2	- 137	- 139.6	no reaction
$MeSnCl_3$	- 21[c]	- 17.5	no reaction

a reference 22; b estimated value; c chloroform solvent; d major peak.

The large range of values found for postulated Me_2SnCl_2 product (- 131.7 to - 146.1) is due to the large concentration dependence of the 4-coordinate organotin halides.

The results indicate that organo-group transfer to Sb, with reciprocal chloride transfer to tin, is taking place rather than chloride abstraction from the organotin chloride and cation formation.

(ii) Isolation and identification of reaction products

Reactions were carried out in an analogous fashion to that described in (i), except that a larger excess of $SbCl_5$ was used. When all effervescence had subsided, the solutions were pumped to dryness (or as near as possible) to ensure complete removal of solvent and excess $SbCl_5$. The remaining product(s) was investigated by ^{119}Sn n.m.r. and conventional techniques. Experimental details are given in section 4, but a summary of the results obtained is outlined in Table 24.

Several conclusions can be drawn from these results. Firstly, since no tin was detected in any of the products isolated from reactions of phenyltinchlorides (or tetraphenyltin) with $SbCl_5$, it can be assumed that complete removal of the phenyl groups occurs, forming $SnCl_4$ as the only tin-containing product. This would then be removed during pumping under vacuum.

The methyl groups of the methyltin halides, however, are less easily removed by $SbCl_5$; $MeSnCl_3$ remains unchanged on reaction, Me_2SnCl_2 and Me_3SnCl exchange only one methyl group, and Me_4Sn exchanges two methyl groups before reaction stops. ^{119}Sn n.m.r. is an extremely useful technique for identifying the tin-containing products formed in these reactions. The only 'peculiar' shift obtained was that from the product of one isolated reaction between Me_3SnCl and $SbCl_5$, which has so far been unreproducible. Although the compound analysed very well for a 2:1 ratio of Me_2SnCl_2 and Me_2SbCl_3, the shift of -235.1 ppm strongly suggests a cationic tin-containing species.

The infra-red spectra of most of the products are contained in Appendix 1, nos. 16-23. The i.r. spectra of the three products proposed to be Ph_2SbCl_3 turned out to be very similar. Although no literature spectrum could be found for comparison, this is what would be expected

TABLE 24 Summary of Products Isolated from Reactions with $SbCl_5$

Starting material	Product Appearance	^{119}Sn Chemical shift (ppm)	Proposed product	Analysis found %	Analysis required %
Me_4Sn	white powdery solid	- 130.3[a]	Me_2SnCl_2 + Me_2SbCl_3 (1:1)	Sn, 22.7; Sb, 25.9; Cl, 35.2; C, 10.8; H, 3.3.	Sn, 24.9; Sb, 25.5; Cl, 37.1; C, 10.0; H, 2.5.
Me_3SnCl	a) off-white crystals	- 132.6[b]	Me_2SnCl_2 + Me_2SbCl_3 (2:1)	Sn, 33.3; Sb, 16.7; Cl, 33.7; C, 10.3; H, 2.9.	Sn, 34.1; Sb, 17.5; Cl, 35.7; C, 10.3; H, 2.6.
	b) orange-red crystals	- 235.1[b]	see text	Sn, 35.7; Sb, 16.1; Cl, 35.3; C, 9.2; H, 2.8.	
Me_2SnCl_2	red liquid at room temp.	- 7.0[b]	$MeSnCl_3$	-	-
$MeSnCl_3$	dark red liquid	- 17.5[b]	$MeSnCl_3$	-	-
Ph_4Sn	white solid	-	Ph_2SbCl_3	Sn, - ; Sb, 28.7; Cl, 26.7; C, 37.5; H, 2.6.	Sn, - ; Sb, 31.9; Cl, 27.8; C, 37.6; H, 2.6.
Ph_3SnCl	off-white solid	-	Ph_2SbCl_3	Sn, - ; Sb, 32.0; Cl, 29.7; C, 37.3; H, 2.6.	Sn, - ; Sb, 31.9; Cl, 27.8; C, 37.6; H, 2.6
Ph_2SnCl_2	off-white solid	-	Ph_2SbCl_3	Sn, - ; Sb, 29.5; Cl, 26.9; C, 35.9; H, 3.0.	Sn, - ; Sb, 31.9; Cl, 27.8; C, 37.6; H, 2.6.
$PhSnCl_3$	grey solid	-	$PhSbCl_4$	Sn, - ; Sb, 35.1; Cl, 41.6 C, 21.1; H, 1.5.	Sn, - ; Sb, 35.8; Cl, 41.6; C, 21.1; H, 1.5.

a CH_2Cl_2 solvent b Solid state or neat liquid

from the conclusions proposed. Similarly, no spectrum of $PhSbCl_4$ could be found in the literature, but the spectrum clearly differs from those proposed to be Ph_2SbCl_3 and Ph_3SbCl_2, and elemental analysis is quite conclusive in this case.

Since mixtures of tin- and antimony-containing products result from reactions between methyltinchlorides (or tetramethyltin) and $SbCl_5$, the i.r. spectra are more complicated, but certain characteristic i.r. bands can still be assigned to particular 4-coordinate methyltin chlorides formed. This information is summarized in Table 25.

TABLE 25 I.r. Data for Products from Reaction between Methyltinchlorides and $SbCl_5$

Starting material	Spectrum of product (cm^{-1})[a]	Proposed product	Infra-red spectrum (cm^{-1})
Me_4Sn	∿330 (sh), 340, 521, 570	Me_2SnCl_2	310, 330, 519, 568
Me_3SnCl[b]	285 (sh), 300–335 (broad hump), 522, 572	Me_2SnCl_2	310, 330, 519, 568
Me_2SnCl_2	∿315-380 (v. broad hump), 544	$MeSnCl_3$	345 (sh), 380, 548
$MeSnCl_3$	∿340, ∿365, ∿380, 550	$MeSnCl_3$	345 (sh), 380, 548

a 250-650 cm^{-1}; b off-white crystals (orange-red crystals could not be made into a mull).

(iii) Reactions with neat $SbCl_5$

Reaction was carried out in the absence of solvent between the organotin chloride and $SbCl_5$. A small amount of organotin chloride was placed in an n.m.r. tube, and ~ 1 cm^3 of neat $SbCl_5$ was cautiously added dropwise. The resulting reactions were generally highly exothermic and in many cases accompanied by the evolution of dense fumes. In all instances, when reaction had subsided, clear solutions remained, which varied in colour between pale yellow and deep brown. The ^{119}Sn n.m.r. spectrum of each sample was then recorded, and the results obtained are summarised in Table 26.

TABLE 26 ^{119}Sn Shifts of Organotin Chlorides in Neat $SbCl_5$

Organotin Halide	^{119}Sn Shift of product (ppm)	Proposed product
Me_3SnCl	- 137.4	Me_2SnCl_2
Me_2SnCl_2	- 20.9	$MeSnCl_3$
$MeSnCl_3$	- 21.0	$MeSnCl_3$
$SnCl_4$	+ 150.1	$SnCl_4$
Ph_4Sn	+ 150.1	$SnCl_4$
Ph_3SnCl	+ 150.1	$SnCl_4$
Ph_2SnCl_2	+ 153.6	$SnCl_4$
$PhSnCl_3$	+ 150.1	$SnCl_4$

These results show that reaction with neat $SbCl_5$ is a much more forcing process compared with a diluted solution in a non-polar solvent. All phenyl groups were completely removed from phenyltinchlorides

$SnCl_4$ being the only tin-containing product formed in each case. In the methyltinchloride series, removal of methyl groups again proved more difficult than phenyl groups; $MeSnCl_3$ dissolved slowly in $SbCl_5$, but no reaction occurred, whereas Me_3SnCl and Me_2SnCl_2 exchanged only one methyl group.

3. Summary and Discussion

The results obtained show that the reaction between an organotin chloride (organo = methyl, phenyl) and antimony pentachloride results in a redistribution of organo-groups between the two starting materials. Under the reaction conditions used, the main products formed in these reactions are listed in Table 27.

TABLE 27 Summary of Reaction Products from Reaction between Organotin Chlorides and $SbCl_5$

Organotin(IV) Chloride	Product with $SbCl_5$		
	In solution	After Product isolation	With neat $SbCl_5$
Me_4Sn	Me_3SnCl, Me_2SnCl_2	Me_2SnCl_2	-
Me_3SnCl	Me_2SnCl_2	Me_2SnCl_2	Me_2SnCl_2
Me_2SnCl_2	no reaction	$MeSnCl_3$	$MeSnCl_3$
$MeSnCl_3$	no reaction	no reaction	no reaction
Ph_4Sn	Ph_2SnCl_2	$SnCl_4$[a]	$SnCl_4$
Ph_3SnCl	$PhSnCl_3$	$SnCl_4$[a]	$SnCl_4$
Ph_2SnCl_2	$PhSnCl_3$, $SnCl_4$	$SnCl_4$[a]	$SnCl_4$
$PhSnCl_3$	$SnCl_4$	$SnCl_4$[a]	$SnCl_4$

a not isolated, but postulated.

Only in one isolated case (which, as mentioned, proved to be unreproducible) was a chemical shift obtained which suggested that a cationic tin complex had formed. This was for the reaction between Me_3SnCl and $SbCl_5$, the product from which had a ^{119}Sn solid state shift of -235.1 ppm. Elemental analysis, however, appeared to contradict this, since the analysis turned out to be very similar to that obtained for products from the same reaction when repeated, products which also gave ^{119}Sn shifts corresponding to Me_2SnCl_2.

The reactions between organotin chlorides and $SbCl_5$ are therefore potentially useful as preparative routes to Ph_2SbCl_3, $PhSbCl_4$, and possibly Me_2SbCl_3.

4. Experimental

Due to the extreme moisture-sensitivity of antimony pentachloride, all reactions were carried out inside the glove box. Organotin chloride starting materials were weighed in stoppered sample bottles outside the glove box, with all adjustments to the weight being made inside the box. A 10 cm^3 measuring cylinder was used for measuring out the approximate amount of $SbCl_5$ required for reaction.

The organotin chloride was completely dissolved in methylene chloride prior to reaction, after which the $SbCl_5$ diluted with the same solvent was carefully added. After stirring for several minutes to ensure complete reaction, a sample was withdrawn if an n.m.r. solution spectrum was required, otherwise all solvent (and any excess $SbCl_5$) was pumped off on the vacuum line. The product was dried by adding a small amount of 30/40 petroleum ether, followed by pumping to dryness, to remove any final traces of methylene chloride. Products were then subjected to spectroscopic investigation and elemental analysis.

The weights of starting materials used in each reaction are listed in Table 28.

TABLE 28 Experiment Details for Reactions between Organotin Chlorides and Antimony Pentachloride

Reaction	Weights of Starting Materials Used
$Me_4Sn + SbCl_5$	Me_4Sn : 0.454 g (2.54 mmol)
	$SbCl_5$: 0.93 g (∿3.12 mmol)
$Me_3SnCl + SbCl_5$	(a) Me_3SnCl : 1.898 g (9.51 mmol)
	$SbCl_5$: 2.90 g (∿9.70 mmol)
	(b) Me_3SnCl : 2.768 g (13.87 mmol)
	$SbCl_5$: 4.67 g (∿15.60 mmol)
$Me_2SnCl_2 + SbCl_5$	Me_2SnCl_2 : 2.320 g (10.51 mmol)
	$SbCl_5$: 3.74 g (∿12.50 mmol)
$MeSnCl_3 + SbCl_5$	$MeSnCl_3$: 3.825 g (16.90 mmol)
	$SbCl_5$: 5.72 g (∿19.00 mmol)
$Ph_4Sn + SbCl_5$	Ph_4Sn : 3.201 g (7.50 mmol)
	$SbCl_5$: 2.43 g (∿8.10 mmol)
$Ph_3SnCl + SbCl_5$	Ph_3SnCl : 2.135 g (5.54 mmol)
	$SbCl_5$: 2.24 g (∿7.49 mmol)
$Ph_2SnCl_2 + SbCl_5$	Ph_2SnCl_2 : 2.885 g (8.40 mmol)
	$SbCl_5$: 3.77 g (∿12.60 mmol)
$PhSnCl_3 + SbCl_5$	$PhSnCl_3$: 3.790 g (12.52 mmol)
	$SbCl_5$: 4.49 g (∿15.00 mmol)

B. Reaction with Boron Trichloride

1. Introduction

Boron trichloride, although not such a powerful Lewis acid as antimony pentachloride, is also nevertheless widely used as a reagent for adduct formation with Lewis bases. Since the reaction of organotin chlorides with $SbCl_5$ resulted in exchange of organo-groups, naturally it was of interest to see whether similar reactions occurred with BCl_3, since the organoboron chlorides are also known compounds.[60-63]

Another advantage of using BCl_3 was that the ^{11}B nucleus is very suitable for study by n.m.r. spectroscopy, since it has a sensitivity of 0.165 relative to the proton, which is quite high. This means that both the tin-containing and boron-containing products can be studied by n.m.r. spectroscopy. The ^{11}B chemical shifts of the organoboron chlorides have been previously recorded, and are listed in Table 29, together with literature references (all shifts are quoted relative to $(MeO)_3B$ external reference).

2. Present Work

The reactions in methylene chloride solvent between organotin chlorides and BCl_3 were investigated. For completeness, tetramethyl- and tetraphenyltin were also studied. The following procedure was adopted for all reactions. A preweighed amount of organotin chloride was dissolved in methylene chloride in a thick-walled 8.4 mm n.m.r. tube connected to the vacuum line via a modified socket joint. This section of the line was sealed off, then the required amount of BCl_3 (in excess of a 1:1 ratio) was condensed into a graduated cold finger at liquid nitrogen temperature (77 K). The n.m.r. tube was then cooled to 77 K, whilst the

TABLE 29 ^{11}B Chemical Shifts for the Organoboron Chlorides and Possible Hydrolysis Products

Compound	^{11}B Shift (ppm)	Reference
BCl_3	- 29.4	63
$MeBCl_2$	- 45.1	63
Me_2BCl	- 59.9	63
Me_3B	- 68.9	63
$PhBCl_2$	- 37.7	63
Ph_2BCl	- 43.9	63
Ph_3B	- 43.1	63
$MeB(OH)_2.H_2O$	- 13.8	60
$PhB(OH)_2$	- 15.2	60
$Me_2B(OH)$	- 36.5	60

cold-finger was slowly allowed to warm up to room temperature, resulting in a gradual condensation of BCl_3 into the n.m.r. tube. When condensation was complete, the n.m.r. tube was sealed, and allowed to warm up slowly to room temperature.

Both the ^{119}Sn and ^{11}B n.m.r. spectra were then recorded, and by comparing the shifts obtained with known shifts of the organotin chlorides and organoboron chlorides, the products formed in each reaction could be identified. These results are shown in Table 30 (below).

The results obtained from the methyltinchloride series are thus straightforward, with no ambiguity in the chemical shifts of the products. Reaction between an excess of Me_4Sn and boron trichloride was also carried out, to see whether dimethylboronchloride or trimethylboron could be formed. The spectrum contained no BCl_3 peak (which had therefore

TABLE 30 ^{119}Sn and ^{11}B Shifts of Products from Reactions between Organotin Chlorides and BCl_3

System	^{119}Sn Chemical shift (ppm)	Tin-Containing product	^{11}B Chemical shift (ppm)	Boron-Containing product
Me_4Sn + excess BCl_3	- 146.7	Me_2SnCl_2	- 29.6	BCl_3
			- 45.8	$MeBCl_2$
Me_4Sn + BCl_3 ($\sim$1.1)	- 140.5	Me_2SnCl_2	- 45.8*	$MeBCl_2$
			- 60.5	Me_2BCl
Me_3SnCl + BCl_3($\sim$1:0.7)	- 167.2	Me_3SnCl	- 44.1	$MeBCl_2$
	- 128.7	Me_2SnCl_2	- 59.3*	Me_2BCl
Me_2SnCl_2 + excess BCl_3	- 142.0	Me_2SnCl_2	- 29.4	BCl_3
$MeSnCl_3$ + excess BCl_3	- 19.8	$MeSnCl_3$	- 28.6	BCl_3
Ph_4Sn + excess BCl_3	+ 64.0	$PhSnCl_3$	- 13.4	$(PhB(OH)_2)$
			- 29.4	BCl_3
			- 38.3	$PhBCl_2$
Ph_4Sn + BCl_3 ($\sim$1:2)	+ 62.7	$PhSnCl_3$	- 38.7	$PhBCl_2/Ph_2BCl$
Ph_3SnCl + excess BCl_3	+ 153.7	$SnCl_4$	- 29.6	BCl_3
			- 37.7	$PhBCl_2$
Ph_2SnCl_2 + excess BCl_3	+ 62.9	$PhSnCl_3$	- 29.6	BCl_3
			- 39.4	$PhBCl_2/Ph_2BCl$
$PhSnCl_3$+ excess BCl_3	+ 146.6	$SnCl_4$	- 28.6	BCl_3
			- 37.7	$PhBCl_2$

* major peak

( ) postulated only (see text).

completely reacted), a major peak corresponding to $MeBCl_2$, and a small peak corresponding to Me_2BCl. The removal of methyl groups, however, ceases at the dimethyl compound, whatever the molar ratio of starting materials.

One or two points from the phenyltinchloride series, however, require some explanation. In the system (Ph_4Sn + excess BCl_3) a small peak appears in the ^{11}B spectrum at - 13.4 ppm. This cannot be assigned to any of the organoboron chlorides, but is quite close to the shift of $PhB(OH)_2$ (lit.[60] - 15.2 ppm); this product may have been formed if a slight leakage of air into the tube had occurred, although it is surprising that the excess BCl_3 in the tube should remain unaffected. This small peak did not appear in the spectrum when excess Ph_4Sn was used. In this case, a broad 'hump' at - 38.7 ppm was observed, which is intermediate between the ^{11}B shifts of $PhBCl_2$[63] (- 37.7 ppm) and Ph_2BCl[63] (- 43.0 ppm). Since an exchanging system is unlikely, the 'hump' must be a combination of the peaks from both phenylboronchlorides. This feature was also present in the ^{11}B-spectrum of the Ph_2SnCl_2/ excess BCl_3 system, where the broad band was centred at - 39.4 ppm. Again, this is probably due to a combination of peaks arising from $PhBCl_2$ and Ph_2BCl.

One surprising feature was illustrated by the systems Ph_4Sn/ excess BCl_3, and Ph_2SnCl_2/excess BCl_3. In both cases, the reaction appeared to stop at $PhSnCl_3$, despite the fact that excess BCl_3 still remained in the tube, since these two compounds are known to react from study of the $PhSnCl_3$/excess BCl_3 system. It may be that further reaction is occurring, but only at a very slow rate, and that a much larger proportion of BCl_3 is required to drive the reaction to completion.

3. Summary and Discussion

The results obtained indicate that BCl_3 reacts with the organotin chlorides in a similar manner to $SbCl_5$. Reaction products result from an exchange of organo-groups from tin with chloride from boron. The ease with which organo-groups are removed varies in the same way as with $SbCl_5$. Methyl groups are much more difficult to remove than phenyl groups; Ph_4Sn and Ph_2SnCl_2 react with BCl_3 to form $PhSnCl_3$; Ph_3SnCl forms $SnCl_4$ (obviously a larger excess of BCl_3 was used in this case), and $PhSnCl_3$ also forms $SnCl_4$. In the methyltinchloride series, however, reaction does not occur with such ease. Me_4Sn exchanges two methyl groups, to form Me_2SnCl_2, while Me_3SnCl exchanges only one methyl group, at which point the reaction stops. Me_2SnCl_2 and $MeSnCl_3$, do not react with BCl_3 under the reaction conditions employed.

4. Experimental

The weights of starting materials (and molar ratios) used in the reactions are listed in Table 31. Where excess Me_4Sn or a higher proportion of Ph_4Sn was used, the amount of BCl_3 added was not measured accurately, although care was taken to ensure that the amount added was known approximately.

TABLE 31 Experimental Details for Reactions between Organotin Chlorides and BCl_3

Organotin Chloride		BCl_3	Approximate Molar Ratio
Me_4Sn	0.243g (1.36 mmol)	0.5 ml (∿0.675g) (∿5.74 mmol)	1:4.2
Me_3SnCl	1.390g (6.97 mmol)	0.4 ml (∿0.540g) (∿4.60 mmol)	1:0.7
Me_2SnCl_2	0.799g (3.63 mmol)	0.4 ml (∿0.540g) (∿4.60 mmol)	1:1.3
$MeSnCl_3$	0.267g (1.11 mmol)	0.3 ml (∿0.405g) (∿3.45 mmol)	1:3.1
Ph_4Sn	0.423g (1.11 mmol)	0.3 ml (∿0.405g) (∿3.45 mmol)	1:3.1
Ph_3SnCl	0.454g (1.18 mmol)	0.35 ml(∿0.473g) (∿4.03 mmol)	1:3.4
Ph_2SnCl_2	0.572g (1.66 mmol)	0.45 ml (∿0.607g) (∿5.17 mmol)	1:3.1
$PhSnCl_3$	0.707g (2.34 mmol)	0.5 ml (∿0.675g) (∿5.74 mmol)	1:2.5

Chapter 5 REACTIONS WITH ACIDIC SOLVENTS: STUDIES BY ^{119}Sn N.M.R.

1. Introduction

Interest in 100% sulphuric acid, oleum and substituted sulphuric acids as solvent systems is the result of a combination of several significant chemical features. These strongly acidic solvents undergo relatively extensive ionic self-dissociation, so the pure acids have quite high specific conductances; electrolyte solutions in these solvents are therefore of quite high ionic strength. Many of the physical properties of the acids indicate extensive association in the liquid. The chemistry of sulphuric acid and related systems (e.g. 25-oleum and chlorosulphuric acid) has not yet been extensively studied, but a sufficient variety of certain classes of compounds has now been investigated for a reasonably systematic account of their behaviour to be given.[64-68]

Sulphuric acid

The high specific conductance of 100% sulphuric acid shows that it is rather extensively self-ionised, mainly due to $H_3SO_4^+$ and HSO_4^- ions formed by autoprotolysis.[69]

$$2\ H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^- \qquad 5(1)$$

The $H_3SO_4^+$ ion is the strongest possible acid and HSO_4^- the strongest possible base of the sulphuric acid solvent system. Sulphuric acid is also slightly self-dissociated into SO_3 and water:

$$H_2SO_4 \rightleftharpoons H_2O + SO_3 \qquad 5(2)$$

Water is almost completely ionised as a base:

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-, \qquad 5(3)$$

whilst SO_3 is completely converted into disulphuric acid, $H_2S_2O_7$, in dilute solutions (and perhaps to smaller amounts of higher polysulphuric acids). Disulphuric acid itself is ionised as a moderately weak acid.

$$H_2S_2O_7 + H_2SO_4 \rightleftharpoons HS_2O_7^- + H_3SO_4^+ \qquad 5(4)$$

Since the ions $H_3SO_4^+$ and HSO_4^- are in equilibrium as a consequence of the autoprotolysis reactions, it follows that the ions H_3O^+ and $HS_2O_7^-$ must also be in equilibrium.

$$2\ H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^- \qquad 5(5)$$

This is called the ionic self-dissociation reaction, and the complete self-dissociation reaction in the sulphuric acid solvent system can be described by the preceding equations. In 100% sulphuric acid, solutes can undergo any of the following processes[69,70]: solvolysis, protonation, dehydration, oxidation, or sulphonation. More extensive reviews of these systems are available[64-69] but this brief summary of the properties of sulphuric acid shows that a variety of interesting reactions can be carried out in this medium. The chemistry of the related oleum solvents is, on the whole, an extension of the chemistry of 100% H_2SO_4, where the effect of the added SO_3 on the reacting system is taken into account. The proportion of disulphuric (and higher polysulphuric) acids increases with the SO_3 content.

Chlorosulphuric Acid

Little interest has been shown in the properties of $HSClO_3$ as a non-aqueous solvent, but it might turn out to be equally as useful as sulphuric acid and fluorosulphuric acid. Paul and co-workers[71] concluded that the mode of solvent dissociation was:

$$2\ HSClO_3 \rightleftharpoons H_2SO_3Cl^+ + SO_3Cl^- \qquad 5(6)$$

The alternative ionisation path:

$$HSClO_3 \rightleftharpoons HSO_3^+ + Cl^- \qquad 5(7)$$

appears to be of little importance, since conductivities of solutions of the Lewis acids $AlCl_3$, $SbCl_3$, and $SnCl_4$ show that they behave as non-electrolytes.[71]

$HSClO_3$ appears to be about 70 times as strongly acidic as sulphuric acid,[72] which together with its relatively high dielectric constant suggests that it is a potentially useful solvent for both inorganic and organic species.

It should be mentioned that disulphuric acid is a stronger acid than either 100% H_2SO_4 or $HSClO_3$, as shown, for example, by more extensive protonation of weak bases.[73] Hence the acid strength falls in the sequence 25-oleum > $HSClO_3$ > 100% H_2SO_4.

Previous work on the reactions of phosphorus compounds with these and related solvents has shown the value of n.m.r. spectroscopy in following reactions such as protonation, sulphonation of aromatic groups, solvolysis, and sometimes polymerisation,[73–78] and it was therefore of considerable interest to extend these studies to tin compounds, using

^{119}Sn n.m.r. spectroscopy as the investigative technique. For phosphorus compounds, solvolysis of halogeno-compounds increases as the acid strength decreases. Hence chloro-compounds tend to solvolyse slowly, if at all, in 25-oleum and $HSClO_3$, but more rapidly in 100% H_2SO_4.

Nomenclature

In the explanations postulated in the remainder of this chapter, the symbol X is used to represent an anionic group from the acid solvent (e.g. HSO_4^-, OH^-, $SClO_3^-$ or even Cl^- from $HSClO_3$), since the actual group involved in solvolysis, etc., cannot be positively identified in these reactions.

2. Present Work

The complete series of methyl- and phenyl-tin chlorides, together with tetramethyl- and tetraphenyltin for completeness, were investigated by ^{119}Sn n.m.r. spectroscopy in each of the three acidic solvents, 100% H_2SO_4, 25-oleum, and chlorosulphuric acid. Spectra were also recorded for $SnCl_4$ and salts containing the $SnCl_5^-$ and $SnCl_6^{2-}$ ions. All reactions were carried out using the same technique; in each case, approximately 1 cm depth of organotin chloride or tin-containing salt was placed in an n.m.r. tube (within the glove box) and the acidic solvent was then added dropwise, with extreme caution. The tube was then left unstoppered until all signs of effervescence had subsided, and the ^{119}Sn n.m.r. spectrum then recorded. In chlorosulphuric acid, clear solutions resulted and reasonable results could be obtained fairly quickly, whereas solids tended to form with the other two more viscous solvents, 100% sulphuric acid and 25-oleum, and overnight runs were often required to obtain reasonable spectra.

(i) 100% H_2SO_4

TABLE 32 Chemical Shifts in 100% Sulphuric Acid

Compound	^{119}Sn Chemical Shift (ppm)
Me_4Sn	+ 226.9
Me_3SnCl	+ 230.4
Me_2SnCl_2	+ 230.4
$MeSnCl_3$	+ 160.6
$SnCl_4$	+ 146.6
$Ph_3C^+.SnCl_5^-$	+ 148.2
$Et_4N^+.SnCl_5^-$	+ 146.6
$2(MeNH_3)^+.SnCl_6^{2-}$	+ 740.9
$2(NH_4)^+.SnCl_6^{2-}$	+ 150.1
Ph_4Sn	+ 885.9
Ph_3SnCl	+ 624.8
Ph_2SnCl_2	+ 624.8
$PhSnCl_3$	+ 148.3

At first glance, these results do not appear to form any obvious pattern, and since the isolation and subsequent identification of any reaction products was not possible, any rationalisation of the results can only be postulatory. The following explanation, however, seems to accord with most of the results obtained.

If the replacement of an organo-group (and perhaps also chloride) by an anion from the acid is assumed, then it appears that in the

methyltinchloride series an exchanging system results, with the tin-containing product being an equilibrium mixture of 4- and 5-coordinate tin species. This is a reasonable assumption, since the resonances for the methyltinchlorides all move upfield, suggesting an increase in coordination number. An upfield shift would also be expected on replacement of methyl and chloride by a more bulky group (probably HSO_4^-); this has been observed in phosphorus n.m.r. studies of aryl-phosphorus compounds, where, for instance, sulphonation of the aryl groups usually causes an upfield shift.[78] This could occur by the following reaction:

$$2\ H_2SO_4 + R\text{-}Sn\langle \longrightarrow R.SO_2OH + HSO_4\text{-}Sn\langle + H_2O \qquad 5(8)$$

(where R = Me or Ph)

The acid formed as a product in the above reaction (methane or benzene sulphonic acid) is of lower strength than sulphuric acid itself. Hence, as replacement of groups on the organotin chloride takes place, the overall acid strength decreases and the possibility of solvolysis is increased. The same situation applies to both methyl- or phenyltin chlorides. This point will be referred to later, particularly with respect to reactions in chlorosulphuric acid.

Since Me_4Sn, Me_3SnCl, and Me_2SnCl_2 all give essentially the same ^{119}Sn n.m.r. shifts in 100% H_2SO_4, it appears that the same species forms in each case; if this is so, replacement of Cl^- as well as Me must be invoked, since there can be no chloride in the product from Me_4Sn. The most probable species formed from these starting materials is $MeSnX_4^-$ (in equilibrium with $MeSnX_3$); the alternative is an SnX_4 / SnX_5^- exchanging system, but the former would seem more likely, as experiments with $SbCl_5$ and BCl_3 have proved the difficulty of removing the last methyl group.

The problem is then the shift of $MeSnCl_3$, which is at much lower field. Either there is more $MeSnCl_3$ in the mixture, which would not be expected from the acceptor properties, or the methyl group is removed, as in equation 5(8).

The shifts of both $SnCl_5^-$ salts are very close to that of $SnCl_4$ (within experimental error) and it appears that loss of Cl^- occurs in both cases, leaving $SnCl_4$ as the only tin-containing product.

Very surprising results were obtained for the two $SnCl_6^{2-}$ salts in 100% H_2SO_4. Ammonium hexachlorostannate appears to form $SnCl_4$ (by loss of two Cl^- ions to the solvent), but the methyl group in the cation of methylammonium hexachlorostannate appears to stabilize the compound with respect to Cl^- loss, and the resulting shift is very close to that of $SnCl_6^{2-}$ in methylene chloride solvent (measured at + 734.6 ppm for $(Pe_4N)_2SnCl_6$).

The phenyltinchlorides form a very similar series to the methyltin chlorides, although with the exception of $PhSnCl_3$, chemical shifts are much higher. It seems certain that 5- and 6-coordinate products are being formed, because of the substantial upfield shifts with respect to the starting materials. If the product from Ph_4Sn is assumed to be SnX_6^{2-}, then by comparison of the shifts obtained, the products from Ph_3SnCl and Ph_2SnCl_2 must either be of lower coordination number (e.g. an exchanging system between a mixture of SnX_6^{2-} and SnX_5^-) or of six fold coordination but containing fewer bulky X-groups. The latter postulate is supported by the fact that both products have identical ^{119}Sn n.m.r. shifts, which would not be expected from exchanging systems unless by a remarkable coincidence. This still leaves several possible formulations for the product. Since its shift is lower than that of $SnCl_6^{2-}$ in 100% H_2SO_4, a

coordination number of 5 is perhaps more likley than 6, unless mixed compounds $Sn(X)_nCl_{6-n}^{2-}$ have shifts lower than both SnX_6^{2-} and $SnCl_6^{2-}$, which appears unlikely. The product probably contains either one or no Cl^- groups, since if there were more than one, the extra chloride groups for Ph_3SnCl would have to be accounted for. This leaves SnX_4Cl^- or SnX_5^- as the most likely possibilities. It would be possible, of course, to generate a product containing more chlorine than the starting material, if other insoluble products containing little or no chlorine precipitated out. Nevertheless, solvolysis from, for example, Ph_3SnCl is likely to be extensive since formation of benzene sulphonic acid will reduce the acid strength, so the postulation of SnX_5^- or SnX_4Cl^- looks reasonable.

$PhSnCl_3$, however, appears to form $SnCl_4$ in 100% sulphuric acid, although if this is the case, there must be some other tin-containing product formed to account for the extra chlorine needed. Of course this could be explained if the other tin-containing products precipitated out of solution as solids (precipitates were formed by most organotin chlorides in 100% H_2SO_4). The reactions in 25-oleum (next section) suggest that this indeed happens, since several products have been identified in solution as containing more chloride than the starting material.

Evidence in favour of X being the same species in 100% H_2SO_4 and 25-oleum (next section) is obtainable from the shift of Ph_4Sn, which is the same in both solvents, and therefore SnX_6^{2-} is proposed to be the same species in both solvents. X is likely to be HSO_4^- rather than OH^- in this case, since the existence of free OH groups in 25-oleum is unlikely. This is also in accordance with the high upfield shift, which is as expected for a bulky group, X. The chemical shift of the sodium salt of $Sn(OH)_6^{2-}$ in water has been previously recorded[26] at + 592 ppm, which is much lower than the shift of Ph_4Sn in 100% H_2SO_4 (or 25-oleum).

(ii) 25-Oleum

TABLE 33 Chemical Shifts in 25-Oleum

Compound	^{119}Sn Chemical Shift (ppm)
Me_4Sn	+ 258.5
Me_3SnCl	+ 243.7
Me_2SnCl_2	+ 242.0
$MeSnCl_3$	+ 663.1
$SnCl_4$	+ 732.3, + 805.6
$Ph_3C^+.SnCl_5^-$	+ 726.1
$Et_4N^+.SnCl_5^-$	+ 150.9, +227.7
$(MeNH_3)_2^+.SnCl_6^{2-}$	+ 725.5
Ph_4Sn	+ 883.0
Ph_3SnCl	(+ 580.0), + 734.5, + 807.9
Ph_2SnCl_2	+ 587.9, 734.5, + 807.9
$PhSnCl_3$	(+ 598.0), 732.0, + 805.4

( ) = very weak signals

As with 100% H_2SO_4, the results do not appear to fall into any particular pattern at first glance, but from the shifts obtained, a number of deductions and postulates are possible.

Each member of the methyltinchloride series yielded a single ^{119}Sn n.m.r. signal which was at higher field than that of the corresponding starting material. The shifts of Me_4Sn, Me_3SnCl and Me_2SnCl_2 were all very similar, suggesting that the same product was formed in each case. Since all three shifts were sited well upfield from the shifts of the starting

materials, an increase in coordination number has probably occurred. The last methyl group is normally very difficult to remove, therefore the most probable product is $MeSnX_4^-$, possibly in equilibrium with $MeSnX_3$, as in the H_2SO_4 systems. A much higher shift, however, was obtained for $MeSnCl_3$, suggesting the formation of a 6-coordinate complex (the reverse of the situation in 100% H_2SO_4, where $MeSnCl_3$ gave a lower shift than the other methyltinchlorides). Results from studies with Lewis acids (Chapter 4) suggest that $MeSnCl_3$ is the most stable of the methyltinchlorides, hence possibly the addition of two anions from the acid has occurred, forming the 6-coordinate complex, $MeSnCl_3X_2^{2-}$. This is not unreasonable, since solvolysis is expected to be slower in this solvent than in 100% H_2SO_4, and $MeSnCl_3$ is the best acceptor, so is more likely to form a six-coordinate species.

$SnCl_4$ yielded a two-peak spectrum, the major peak at +732.3 ppm corresponding to $SnCl_6^{2-}$, and a peak of lower intensity at + 805.6 ppm, probably due to a 6-coordinate complex containing a mixture of chloride ions and anions from the solvent, X^-. If solvolysis does not occur, the most probable species for this latter peak is $SnCl_4X_2^{2-}$, with the excess tin being precipitated in the form of an insoluble solid (such as stannic oxide or an oxo-complex). In an attempt to verify this, 25-oleum (and $HSClO_3$) were separately added to n.m.r. tubes containing stannic oxide. No observable reaction occurred (the oxide appeared to be completely insoluble) and no ^{119}Sn n.m.r. signals were obtained.

Very different shifts were obtained for the two $SnCl_5^-$ salts investigated. $Ph_3C^+SnCl_5^-$ yielded a single peak at + 725.1 ppm, which is close to the solution shift of $SnCl_6^{2-}$, and upfield from the shift of the parent compound in nitromethane solvent (measured at + 651.7 ppm). Formation of $SnCl_6^{2-}$ requires that another tin-containing product be

formed (to account for the extra chloride) which must be precipitated out with the insoluble residues. $Et_4N^+SnCl_5^-$, however, appeared to lose Cl^- to form $SnCl_4$ (shift + 150.9 ppm). A broad band at ∿ + 227.0 ppm was also observed in the spectrum, possibly due to some tin-containing solid residue. Both these peaks are downfield from the shift of $Et_4N^+SnCl_5^-$ in nitromethane solvent (measured at + 501.7 ppm).

Methylammonium hexachlorostannate appeared to be unchanged in 25-oleum, as was the case in 100% H_2SO_4.

The phenyltinchlorides form a more interesting series, since apart from Ph_4Sn, each has a ^{119}Sn n.m.r. spectrum containing more than one peak. As previously mentioned, the shift of Ph_4Sn is the same as in 100% H_2SO_4, indicating that the same SnX_6^{2-} species had been formed. Since this peak did not appear in the spectra of the other three phenyltinchlorides, it can be assumed that this product was not formed from these starting materials. Ph_3SnCl yielded a major peak at + 807.9 ppm, with two weaker peaks at + 734.5 ppm and + 580.0 ppm. The 734.5 ppm peak can probably be assigned to $SnCl_6^{2-}$, and by analogy with $SnCl_4$, which also yielded a peak at + 805.6 ppm, the major peak can be assigned to a 6-coordinate mixed-anion species, probably $SnCl_4X_2^{2-}$. To rationalize the extra chloride ion needed for formation of these products, a substantial amount of tin-containing solid with no chloride involved must be contained in the precipitate. The peak at ∿ 580 ppm can probably be assigned to a 5-coordinate complex, possibly $SnCl_3X_2^-$, since the peak appears in the spectrum of $PhSnCl_3$, and in this case a) solvolysis is unlikely, and b) the product is unlikely to contain any phenyl groups.

The ^{119}Sn n.m.r. spectrum of Ph_2SnCl_2 contained the same three peaks, but the intensity ratios were somewhat different, the peaks at + 734.5 ppm and + 587.9 ppm being of higher relative intensities with

respect to the major peak at + 807.9 ppm. Formation of a larger proportion of $SnCl_6^{2-}$ would be expected, since the starting material contains proportionately more chlorine. This trend was continued with $PhSnCl_3$, where the $SnCl_6^{2-}$ peak was now the major peak. The peak at + 598.0 ppm was again of very low intensity, not surprisingly since $PhSnCl_3$ is a very powerful acceptor, and hence more 6-coordinate product would be expected.

The results for the phenyltinchlorides, therefore, generally suggest that all phenyl-groups are displaced on reaction with 25-oleum.

(iii) Chlorosulphuric Acid, $HSClO_3$

TABLE 34 Chemical Shifts in $HSClO_3$ Solvent

Compound	^{119}Sn Chemical Shift (ppm)
Me_4Sn	+ 83.8
Me_3SnCl	+ 104.3
Me_2SnCl_2	+ 7.0
$MeSnCl_3$	+ 7.0
$SnCl_4$	+ 149.3
$Ph_3C^+.SnCl_5^-$	+ 176.5
$Et_4N^+.SnCl_5^-$	+ 234.7
$2NH_4^+.SnCl_6^{2-}$	+ 183.9
Ph_4Sn	+ 164.8
Ph_3SnCl	+ 161.3
Ph_2SnCl_2	+ 157.9
$PhSnCl_3$	+ 157.9

The chemical shifts in chlorosulphuric acid solvent differed generally from those in 100% H_2SO_4 or 25-oleum in that they appeared at much lower field in most cases. The major difference between the solvents is that in the case of $HSClO_3$, Cl^- (and $SClO_3^-$) are available as anions, being formed according to equation 5(9):

$$SClO_3^- \rightleftharpoons Cl^- + SO_3 \qquad 5(9)$$

The shifts of the methyltinchloride series all occurred in the region between the shifts of starting materials and that of $SnCl_4$. This suggests that the shift is an exchange peak resulting from rapid exchange between, say, $MeSnCl_3$ and $SnCl_4$, since the last methyl group is normally difficult to remove. This would account for the fact that Me_2SnCl_2 and $MeSnCl_3$ gave the same chemical shift in $HSClO_3$, but does not reconcile with the unusual shift sequence when compared with that of the starting materials, since a shift much closer to that of $MeSnCl_3$ would be expected. The reaction which takes place presumably involves:

$$Me\text{-}Sn\!\!\!\diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown + HSClO_3 \longrightarrow Cl\text{-}Sn\!\!\!\diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown + (Me)HSO_3 \qquad 5(10)$$

methane sulphonic acid

To prove that a mixture of starting materials in $HSClO_3$ would give an exchange peak rather than separate signals, a mixture of Me_3SnCl and $SnCl_4$ in $HSClO_3$ was investigated by ^{119}Sn n.m.r. and the spectrum consisted of a major peak at + 12.8 ppm with a much weaker peak at + 159.9 ppm. The latter probably arises from replacement of chloride or methyl by a bulkier group (X) from the acid, but the major peak clearly proves that an exchanging system does exist in this particular solvent.

Since methane sulphonic acid is weaker than chlorosulphuric acid, solvolysis is increasingly likely to occur as the concentration of the former rises. This could account for the higher shifts upfield of Me_4Sn and Me_3SnCl relative to Me_2SnCl_2 and $MeSnCl_3$; with the former two starting materials, the percentage of methane sulphonic acid would be greater, which increases the possibility of solvolysis, giving more X groups in the product.

$SnCl_4$ itself appears to remain unchanged in chlorosulphuric acid. The two $SnCl_5^-$ salts each yielded a single peak, at 176.5 ppm for the Ph_3C^+ salt, and at + 234.7 ppm for the Et_4N^+ salt. This suggests some form of exchanging system, between $SnCl_4$ and $SnCl_5^-$, and hence partial dissociation of the $SnCl_5^-$ ion. $(NH_4)_2SnCl_6$ yielded a single peak at + 183.9 ppm, again suggesting an exchanging system, with the equilibrium lying heavily on the side of $SnCl_4$, i.e.

$$SnCl_4 \rightleftharpoons SnCl_5^- \rightleftharpoons SnCl_6^{2-} \qquad 5(11)$$

All four members of the phenyltinchloride series yielded very similar shifts in $HSClO_3$, around 160 ppm. This is slightly higher than the shift of $SnCl_4$ itself, and may be accounted for by postulating the complete removal of all phenyl groups to form $SnCl_4$, which then exists in equilibrium with a very small amount of $SnCl_5^-$.

3. Summary and Conclusions

Despite the fact that no products were isolable from the reaction media in these experiments, the information gained from ^{119}Sn n.m.r. investigations allowed a number of reasonable assumptions to be made, especially concerning the probable coordination numbers of the tin-containing products.

It appears that in 100% H_2SO_4, the methyltinchlorides either form an exchanging system between 4- and 5-coordinate tin, or undergo ligand replacement by bulkier ligands derived from the solvent. Both of these possibilities would account for an upfield movement of the n.m.r. signal. A similar situation was found with the phenyltinchlorides, except that the chemical shifts were generally much further upfield, suggesting sixfold coordination about tin, with replacement of phenyl (and probably also chloride) with bulkier ligands from the solvent. In each case, only a single tin-containing product was detected in the solution n.m.r. spectrum.

Results for the methyltinchloride series in 25-oleum were similar to those in 100% H_2SO_4; upfield shifts were obtained for each product, again suggesting either an exchange intermediate between 4- and 5-coordinate tin, or a product where ligands of greater bulk have replaced the existing ones. A surprisingly high shift was obtained for methyltin trichloride, suggesting a six-coordinate product, possibly by addition of two anionic ligands from the acid. The phenyltinchloride series, however, yielded more interesting spectra in that, with the exception of Ph_4Sn, which gave the same shift as in 100% H_2SO_4, each member yielded a 3-peak spectrum. These peaks were assigned, firstly to $SnCl_6^{2-}$, secondly to a six-coordinate anionic complex $SnCl_4X_2^{2-}$ containing a mixture of chloride ligands and ligands from the acid, and thirdly to a 5-coordinate anionic complex.

A different series of shifts was obtained in chlorosulphuric acid solvent, where again only one tin-containing product was detected in the spectrum of each compound. The methyltinchloride series was proposed to form exchanging systems between the starting material and $SnCl_4$ (since chlorosulphuric acid is itself capable of generating Cl^- as a ligand). All four members of the phenyltinchloride series gave single shifts, slightly upfield from the shifts of $SnCl_4$. This may be rationalized by proposing that $SnCl_4$ is formed by replacement of all phenyl groups, which then forms an equilibrium with a small amount of $SnCl_5^-$ due to the excess chloride ion available from the solvent.

4. Experimental

All n.m.r. sample tubes were prepared within the glove box, due to the extreme moisture sensitivity of the acidic solvents used. Tubes were prepared in the manner described in section 2 (Present Work) and the ^{119}Sn n.m.r. spectra were then recorded. Spectra of all samples in chlorosulphuric acid could be obtained reasonably quickly (usually about 1000 pulses being required), whereas with the more viscous solvents 100% sulphuric acid and 25-oleum, overnight runs were usually required. Solid precipitates also tended to form in the latter two solvents.

Chapter 6 FORMATION OF NEUTRAL ADDUCTS WITH MONO- AND BIDENTATE NITROGEN BASES

1. Introduction

An account of the types of complex formed between the organotin chlorides and nitrogen bases, together with literature references is given in Chapter 1, and is summarised below.

Many of the organotin halides behave as Lewis acids, like the tin(IV) halides themselves, and many different types of coordination complex are known.[79] Although the tetraorganotin species are unable to form stable complexes in which tin has a coordination number greater than four, the introduction of one halogen atom on tin is sufficient to produce a Lewis acid which can form complexes with even relatively weak donor bases.

The Lewis acidity of the organotin halides increases considerably with higher halogen content. Thus R_3SnX compounds will react with pyridine to form a five-coordinate, 1:1 complex, $R_3SnX.py$, but addition of another pyridine molecule, or reaction with a bidentate base to form a 6-coordinate complex, does not occur. The di- or mono-alkyl or aryl tin halides, however, will add either 1 or 2 moles of pyridine to form 1:1 or 1:2 complexes, and also form 1:1, 6-coordinate complexes by reaction with bidentate bases such as phen or dipy. The resulting adducts are white, stable solids, which are very resistant to hydrolysis.

By the use of ^{119}Sn n.m.r. it should thus be possible to show that adduct formation has taken place, since an increase in coordination about tin causes increased shielding of the ^{119}Sn nucleus, and subsequently an upfield movement of the chemical shift.

2. Present Work

(a) Preparation and characterisation of products

Essentially the same practical method was used in the preparation of each adduct.

All weighings of starting materials were carried out in stoppered sample bottles outside the glove box, with any alterations to the weight being performed inside the box. Starting materials were weighed to the correct required stoichiometric ratios (either 1:1 or 1:2, depending on the adduct being prepared) and were then dissolved separately in a non-polar solvent. When these two solutions were combined, precipitation of a white amorphous solid was usually instantaneous. The resultant solid was then isolated by filtration, washed with petroleum ether, then dried in vacuo. The exceptions to this were the pyridine adducts of triorganotin chlorides, which were soluble in non-polar solvents. In this case, the products were isolated by pumping off all traces of solvent via the vacuum line.

The infra-red spectra of all adducts formed (range ca. 1200 - 250 cm^{-1}) are included in Appendix 1 (nos. 24-37). In the majority of cases, literature spectra were available for comparison (refs. 12, 15, 26, 80, 81), and good agreement was found between these and the actual spectra obtained. Elemental analyses obtained for each adduct are listed in Table 35 (below), and weights of starting materials used, etc., are tabulated in Section 4 of this chapter. Raman spectra of the adducts are listed in Appendix 2, (nos. 10-23). In each case, the spectrum of the product differed from the combined spectra of starting materials, proving that adduct-formation had taken place.

TABLE 35 Analytic Data for Adducts formed with Py, Phen, and Dipy

Adduct	Analysis Found %	Analysis Required %
$MeSnCl_3.py_2$	Sn, *; Cl, 26.7; C, 33.1; H, 3.6; N, 7.1.	Sn 29.9; Cl, 26.7; C, 33.1; H, 3.3; N, 7.0.
$MeSnCl_3$.dipy	Sn, 27.3; Cl, 25.5; C, 32.5; H, 3.4; N, 6.6.	Sn, 30.0; Cl, 26.7; C, 33.3; H, 2.8; N, 7.1.
$MeSnCl_3$.phen	Sn, 26.0; Cl, 23.4; C, 37.4 H, 2.9; N, 6.4.	Sn, 28.3; Cl, 25.3; C, 37.1; H, 2.6; N, 6.7.
$Me_2SnCl_2.py_2$	Sn, *; Cl, 19.1; C, 38.0; H, 4.6; N, 7.5.	Sn, 31.5; Cl, 18.8; C, 38.1; H, 4.2; N, 7.4.
Me_2SnCl_2.dipy	Sn, 29.9; Cl, 19.5; C, 37.7; H, 3.9; N, 6.7.	Sn, 31.6; Cl, 18.9; C, 38.3; H, 3.7; N, 7.4.
Me_2SnCl_2.phen	Sn, 30.0; Cl, 17.2; C, 41.5; H, 4.1; N, 7.3.	Sn, 29.8; Cl, 17.7; C, 42.0; H, 3.5; N, 7.0.
Me_3SnCl.py	Sn,*; Cl, 12.6; C, 34.5; H, 5.7; N, 4.9.	Sn, 42.7; Cl, 12.7; C, 34.5; H, 7.2; N, 5.0.
$PhSnCl_3.py_2$	Sn, *; Cl, 23.5; C, 42.1; H, 3.2; N,6.5.	Sn, 25.8; Cl, 23.1; C, 41.7; H, 3.3; N, 6.1.
$PhSnCl_3$.dipy	Sn, *; Cl, 24.0; C, 42.3; H, 3.0; N, 6.1.	Sn, 26.0; Cl, 23.2; C, 41.9; H, 2.8; N, 6.1.
$PhSnCl_3$.phen	Sn, 23.2; Cl, 22.0; C, 44.1; H, 3.0; N, 5.7.	Sn, 24.7; Cl, 22.1; C, 44.8; H, 2.7; N, 5.8.
$Ph_2SnCl_2.py_2$	Sn, *; Cl, 14.6; C, 53.9; H, 4.0; N, 5.6.	Sn, 23.7; Cl, 14.1; C, 52.6; H, 4.0; N, 5.6.
Ph_2SnCl_2.dipy	Sn, 22.9; Cl, 15.2; C, 51.3; H, 3.5; N, 5.2.	Sn, 23.8; Cl, 14.2; C, 52.8; H, 3.6; N, 5.6.
Ph_2SnCl_2.phen	Sn, 20.7; Cl, 15.7; C, 52.4; H, 4.0; N, 5.0.	Sn, 22.7; Cl, 13.6; C, 55.0; H, 3.4; N, 5.3.
Ph_3SnCl.py	Sn, *; Cl, 8.3; C, 60.2; H, 4.2; N, 4.3.	Sn, 25.6; Cl, 7.6; C, 59.4; H, 4.3; N, 3.0.

* Several compounds (particularly py adducts) yielded very unsatisfactory tin analyses. The problems were concerned mainly with loss of tin (in the form of volatile halides) during the acid decomposition stage of the analysis. Where this has obviously occurred, no figure is quoted for tin.

(b) ^{119}Sn n.m.r. spectroscopy

^{119}Sn n.m.r. is potentially a very useful technique for study of tin-containing adducts, and for proving adduct formation, since this would result in an upfield movement of the chemical shift. The problems encountered in its application, however, were largely of a practical nature; with the exception of the triorganotin chloride adducts, it was not possible to find a solvent in which the adducts were more than sparingly soluble. The solubilities in the low-polarity solvents used in preparing the adducts were obviously very low indeed, therefore much more polar solvents, such as nitrobenzene, nitromethane, toluene, and pyridine were utilized in an attempt to dissolve enough adduct for an n.m.r. spectrum to be obtained.

Sample n.m.r. tubes were prepared inside the glove box as follows. Approx. 2 cm^3 of solvent was added to about 1 cm depth of solid adduct in the tube, followed by a 5-minute period of continuous shaking. No observable dissolution of solid occurred, and despite overnight runs, during which a minimum of 32,000 pulses at two-second intervals were employed, no signals were detectable in the resulting spectra. The exception to this (and indeed the only solvent in which any measure of success was achieved) was pyridine, from which definite signals were obtained for three of the six diorganotin dichloride adducts.

Since adduct solubility decreases as the number of chlorines on the original organotin chloride increases, it is not surprising that no solution spectra could be obtained for any of the methyl- or phenyltin trichloride adducts. Long weekend catting runs on solid samples of these, and diorganotin dichloride adducts were attempted, accumulating as many as 100,000 pulses in some cases, but again, no signals were detected in the resulting spectra. The fact that all samples were amorphous powders

rather than crystalline solids may be less favourable for obtaining signals, but problems with relaxation times are more likely to be responsible for their non-observation.

The adducts formed between the triorganotin chlorides and pyridine were very soluble, even in non-polar solvents, and reasonable spectra were easily recorded for these adducts. ^{119}Sn n.m.r. shifts which were obtained for the neutral adducts are listed in Table 36.

TABLE 36 ^{119}Sn Chemical Shifts for neutral adducts of organotin chlorides

Adduct	Solvent	$\delta(^{119}Sn)$ / ppm.
$Ph_2SnCl_2.py$	pyridine	+ 387.1
$Ph_2SnCl_2.dipy$	pyridine	+ 378.4
$Me_2SnCl_2.phen$	pyridine	+ 109.5
$Me_3SnCl.py$	CH_3Cl	- 26.0
	CH_2Cl_2	- 24.5
	CH_3NO_2	- 27.9
$Ph_3SnCl.py$	CH_2Cl_2	+ 136.9
	CH_3NO_2	+ 146.7
	$CHCl_3$	+ 90.8
	MeOH	+ 181.6

These chemical shifts are all upfield relative to the 4-coordinate organotin chloride parent compounds, as expected from an increase in coordination about tin.

Since replacement of dipy in $Ph_2SnCl_2.dipy$ by two pyridine ligands from the solvent is considered unlikely, the two adducts, $Ph_2SnCl_2.dipy$

and $Ph_2SnCl_2.py_2$ are seen to have very similar chemical shifts in pyridine solvent. This is perhaps not surprising, since two pyridine ligands or a single dipy ligand ought to have a similar influence on the ^{119}Sn nucleus. The similarity of the shifts, however, suggests that the same type of isomer may form in both cases; this would require the two pyridine ligands to add in a cis-manner, since a dipy ligand can only occupy adjacent (cis) sites on the molecule to which it coordinates. In support of the chemical shifts being similar for $Ph_2SnCl_2.py_2$ and Ph_2SnCl_2.dipy, an analogous situation is found in phosphorus chemistry.[82] The solid state ^{31}P n.m.r. shifts of a number of pyridine-base complexes of the tetrachloro-phosphonium ion were recorded, and the shifts of the py, phen, and dipy complexes were also found to be very similar (see Table 37 below).

TABLE 37 ^{31}P Chemical Shifts for solid complexes $[PCl_4.L_2]$ $[SbCl_6]$ (L = py, ½dipy, ½phen)

L	δ (^{31}P) / ppm.
py	188.2 ± 3.8
phen	184.6 ± 2.2
dipy	191.2 ± 3.3

For the pyridine adduct of the PCl_4^+ ion, n.q.r. has suggested a trans- rather than a cis-structure, whereas the adduct $Ph_2SnCl_2.py_2$ has been postulated[83] to have a cis-dipyridine trans-diphenyl structure (from investigation of the vibrational spectrum) analogous to $Me_2SnCl_2.py_2$.[84]

For Me_2SnCl_2.phen, a ^{119}Sn chemical shift of + 109.5 ppm appears

to be reasonable for a six-coordinate neutral complex, since although the shift of this adduct has not been recorded previously, a complex having the formula $Me_2SnCl_2.2D.M.S.O.$ has been investigated by ^{119}Sn n.m.r.,[20] and yielded a shift at + 84 ppm in satd. CH_2Cl_2.

Also worthy of note is the trend in chemical shifts in going from the 4-coordinate, Me_2SnCl_2 (- 137 ppm), through the 6-coordinate neutral adduct Me_2SnCl_2. phen (+ 109.5 ppm), to the 6-coordinate anionic complex, $(Me_2SnCl_4)^{2-}$ (+ 167 ppm). This upfield movement in chemical shift reflects an increase in electron-density around the tin-atom. Surprisingly, though, the same trend is not repeated in the diphenyltin dichloride series. Both neutral adducts and the proposed anionic 6-coordinate complex $[Ph_2SnCl_4]^{2-}$ have shifts much further upfield from the starting material, but in this case, the shifts of the neutral adducts are slightly (but not significantly) higher than that of the anionic complex. The latter would be expected to have a higher field shift because of greater electron density, so clearly other factors must be influencing chemical shifts in the neutral adducts.

The shifts obtained for the proposed adduct, $Me_3SnCl.py$, are of the right order of magnitude for a 5-coordinate neutral adduct, and the shift in chloroform solvent (-26.0 ppm) agrees favourably with the literature value[19] of -25.4 ppm. The shifts in CH_2Cl_2, and nitromethane suggest a slight solvent dependence of chemical shift, although the results are similar enough for intrinsic error to be responsible for any discrepancy.

The shifts obtained for $Ph_3SnCl.py$ vary widely from one solvent to another, although all shifts are upfield from that of the 4-coordinate parent compound. The large variation in chemical shift probably indicates that $Ph_3SnCl.py$ is less stable in solution than $Me_3SnCl.py$, and the degree of dissociation of the former depends on the solvent.

(c) ^{35}Cl N.q.r. studies

The solid-state ^{35}Cl n.q.r. spectra of all adducts were run, from ∿30 MHz down to ∿10 MHz at 77K, but in all cases, no observable signals were detected. One explanation for this (apart from the fact that n.q.r. spectroscopy is intrinsically a very insensitive technique) is that all samples were in the form of amorphous powders, which are much less favourable than crystalline solids for n.q.r. work. Due to possible adduct instability at elevated temperatures, annealing of samples was not attempted.

3. Summary and Discussion

As previously stated, few positive results were obtained from this investigation, due to the majority of adducts formed being too insoluble for solution n.m.r. studies. Solid state n.m.r. was also attempted, but no signals were detected. The ^{119}Sn shifts which were obtained all reflected the increase in coordination number of tin, since signals appeared at much higher field relative to the parent compounds. The upfield shift on formation of the neutral adduct, Me_2SnCl_2.phen, was less than when the corresponding anionic complex, $[Me_2SnCl_4]^{2-}$ was formed. This was also the case with the 5-coordinate adducts, and is expected on the basis of shielding of the ^{119}Sn nucleus, which would be greater in an anionic complex than a neutral complex of the same coordination number, because the negative charge on the former will increase the electron density about tin. Similar behaviour has been observed in 6-coordinate neutral and anionic phosphorus(V) complexes.[82,85] Surprisingly, the same situation was not encountered with the neutral adducts of Ph_2SnCl_2, since their chemical shifts were slightly higher than the shift of $[Ph_2SnCl_4]^{2-}$.

4. Experimental

TABLE 38 Experimental Data for the Preparation of Neutral Adducts of Organotin Chlorides

Adduct	Organotin Chloride g (mmol)	Ligand g (mmol)	Solvent	Means of Purification
$MeSnCl_3.py_2$	1.111 (4.62)	0.730 (9.24)	CH_2Cl_2	Sublimation on an acetone/CO_2 cold finger at ∿110°C under vacuum
$MeSnCl_3$.dipy	1.743 (7.25)	1.120 (7.18)	CH_2Cl_2	Washing with petroleum ether
$MeSnCl_3$.phen	0.692 (2.88)	0.519 (2.88)	CS_2	-"-
$Me_2SnCl_2.py_2$	0.954 (4.33)	0.685 (8.67)	benzene	-"-
Me_2SnCl_2.dipy	0.711 (3.23)	0.504 (3.23)	CH_2Cl_2	-"-
Me_2SnCl_2.phen	2.160 (9.80)	1.770 (9.80)	CH_2Cl_2	-"-
Me_3SnCl.py	1.442 (7.23)	excess pyridine	30-40° pet. ether	—
$PhSnCl_3.py_2$	0.720 (2.38)	0.376 (4.76)	CH_2Cl_2	Washing with petroleum ether
$PhSnCl_3$.dipy	0.469 (1.55)	0.242 (1.55)	CH_2Cl_2	-"-
$PhSnCl_3$.phen	0.566 (1.87)	0.337 (1.87)	CH_2Cl_2	-"-
$Ph_2SnCl_2.py_2$	1.650 (4.80)	0.756 (9.57)	benzene	-"-
Ph_2SnCl_2.dipy	1.549 (4.50)	0.702 (4.50)	CH_2Cl_2	-"-
Ph_2SnCl_2.phen	0.882 (2.56)	0.462 (2.57)	CH_2Cl_2	-"-
Ph_3SnCl.py	0.863 (2.21)	excess pyridine	CH_2Cl_2	—

Chapter 7 CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The application of ^{119}Sn n.m.r. spectroscopy to the study of reactions of organotin halides in solution in most cases provided useful evidence on the course of reaction, and helped considerably in identifying reaction products.

The reaction of organotin halides (halide = Cl, Br; organo = Ph, Me) with halide ion was successfully investigated, since the majority of systems studied were soluble in common organic solvents. Tetraorganotin compounds were found to display no Lewis acidity in solution, and halide addition did not occur, even to a small extent. Triorganotin halides added only one halide ion, to form 5-coordinate complexes, whereas diorganotin dichlorides (and dibromides) and organotin trichlorides formed 6-coordinate dianionic complexes, by addition of two halide ions. In the latter two cases, between particular starting material:halide ion ratios, the existence of a 5-coordinate intermediate complex was detectable by solution ^{119}Sn n.m.r. Since limited time was available, it was not possible to study all the systems, so there remains scope for further investigation. Work on the organotin bromide / bromide ion systems still remains, and it would be of interest to extend the investigation to the organotin iodides, particularly with regard to studying trends in Lewis acidity.

An investigation into the reactions between organotin chlorides and the powerful Lewis acids, $SbCl_5$ and BCl_3 produces very conclusive results. ^{119}Sn n.m.r. spectroscopy was particularly useful in this case, as all tin-containing reaction products could be identified in solution. ^{11}B n.m.r. was also successfully applied to the study of closed reaction systems where BCl_3 was the Lewis acid, and both the Sn-containing and

B-containing products could be identified in solution. With both Lewis acids, the general reaction occurring was exchange between the organic groups on the tin-compounds and chloride ions from the acid. Phenyl groups were found to be more easily exchanged than methyl groups, and $MeSnCl_3$ proved to be totally inert towards $SbCl_5$ and BCl_3.

The provision of ^{121}Sb facilities would be extremely useful for closer investigation of reactions between $SbCl_5$ and organotin chlorides. The ^{121}Sb nucleus has a natural abundance of 57.25%, and has a high relative sensitivity (0.16 that of the proton for equal numbers of nucleii, hence approximately 0.1 at natural abundance). These factors make the ^{121}Sb nucleus more suitable for n.m.r. study than ^{119}Sn, but the main disadvantage of the former is that I = 5/2; in uncoupled systems, however, this may only lead to some line broadening, as in ^{11}B n.m.r., where I = 3/2.

Reactions of this type may turn out to be potential preparative routes for some of the organoantimony chlorides.

Reactions between the organotin chlorides and 3 acidic solvents, 100% H_2SO_4, 25-oleum, and chlorosulphuric acid were investigated by ^{119}Sn n.m.r. In each system studied, chemical shifts were readily obtained, but assignment proved quite complicated in a lot of cases, and several assumptions had to be made. Difficulties arose because product isolation was not possible, and the only evidence available was the chemical shift data, but it was still possible for reasonable explanations of the majority of reactions to be given. A possible extension of this investigation, which may yield further useful evidence, would be the preparation of some of the proposed products and the recording of their ^{119}Sn n.m.r. spectra in the relevant acidic solvent(s). The observance of any coincidences in chemical shift may help to confirm the assumptions made previously.

An investigation of the neutral adducts formed between organotin chlorides and the nitrogen bases, phen, dipy, and py by ^{119}Sn n.m.r. proved disappointing on the whole, as relatively few positive results were obtained. The problems encountered were chiefly of a practical nature, as the adduct solubilities in the polar solvents tried were too low for signals to be detected in the solution spectra. The shifts which were obtained were upfield relative to the parent compounds, reflecting an increased coordination about tin.

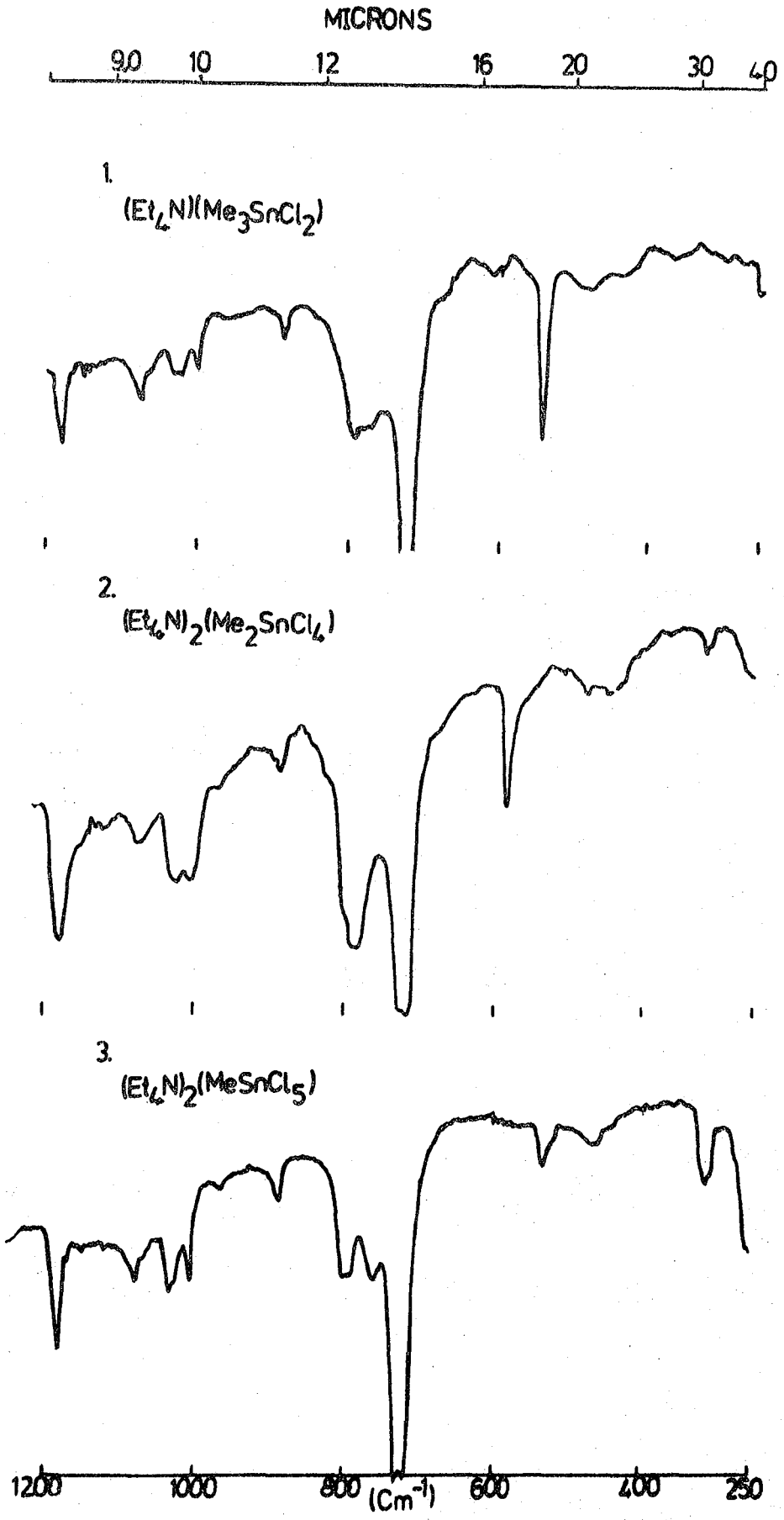
Potentially, this investigation could yield a very interesting series of shifts for these adducts. Clearly, a much more sensitive n.m.r. instrument would be required to obtain signals from these compounds, assuming that a solvent in which they dissolve sufficiently without dissociation cannot be found. If there are relaxation time problems, varying the pulse interval may aid signal enhancement, but there was not sufficient time to investigate this fully.

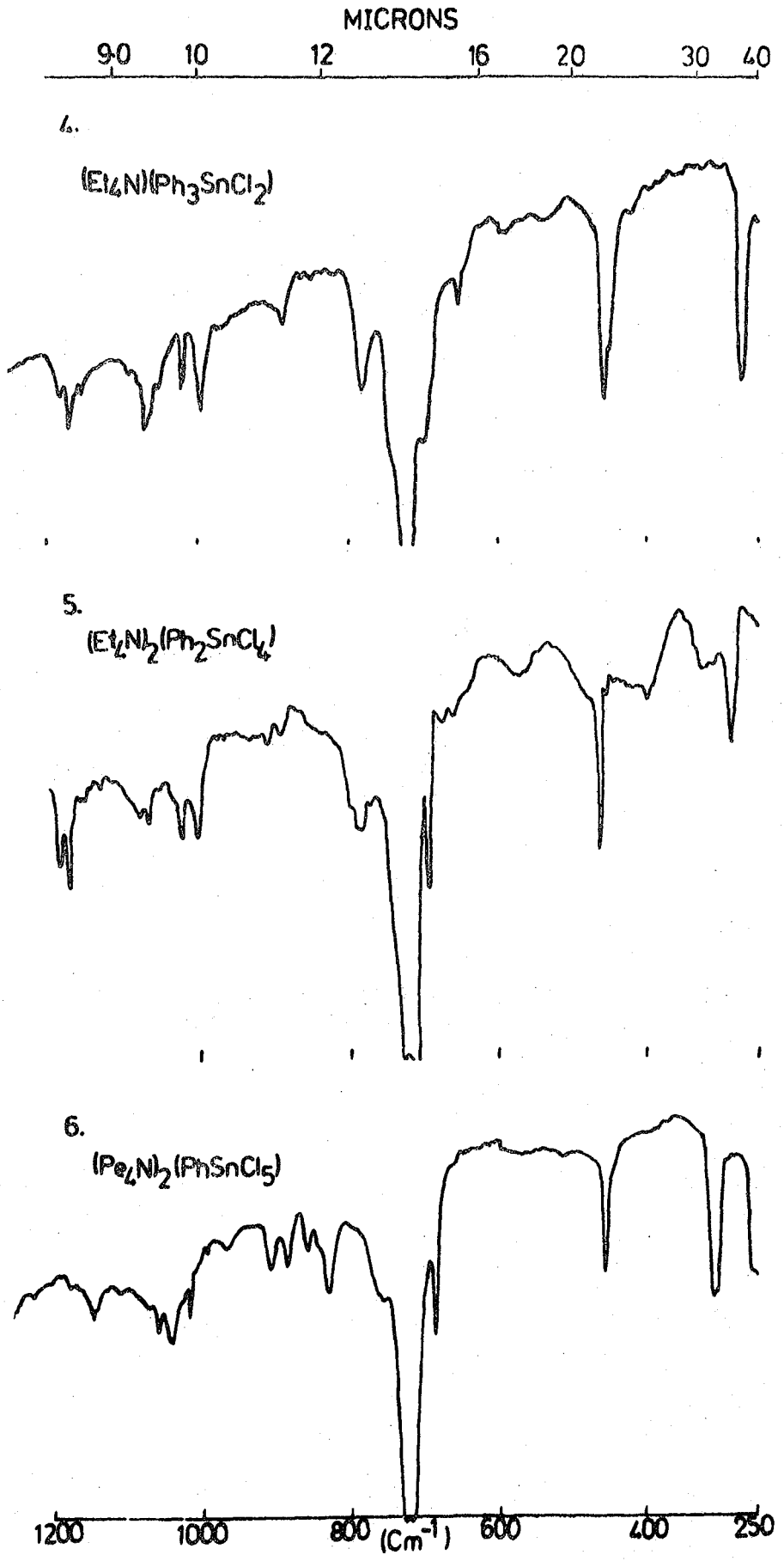
If signals could be obtained successfully, the study could be extended to a whole range of other adducts, and to other organotin halide acceptors.

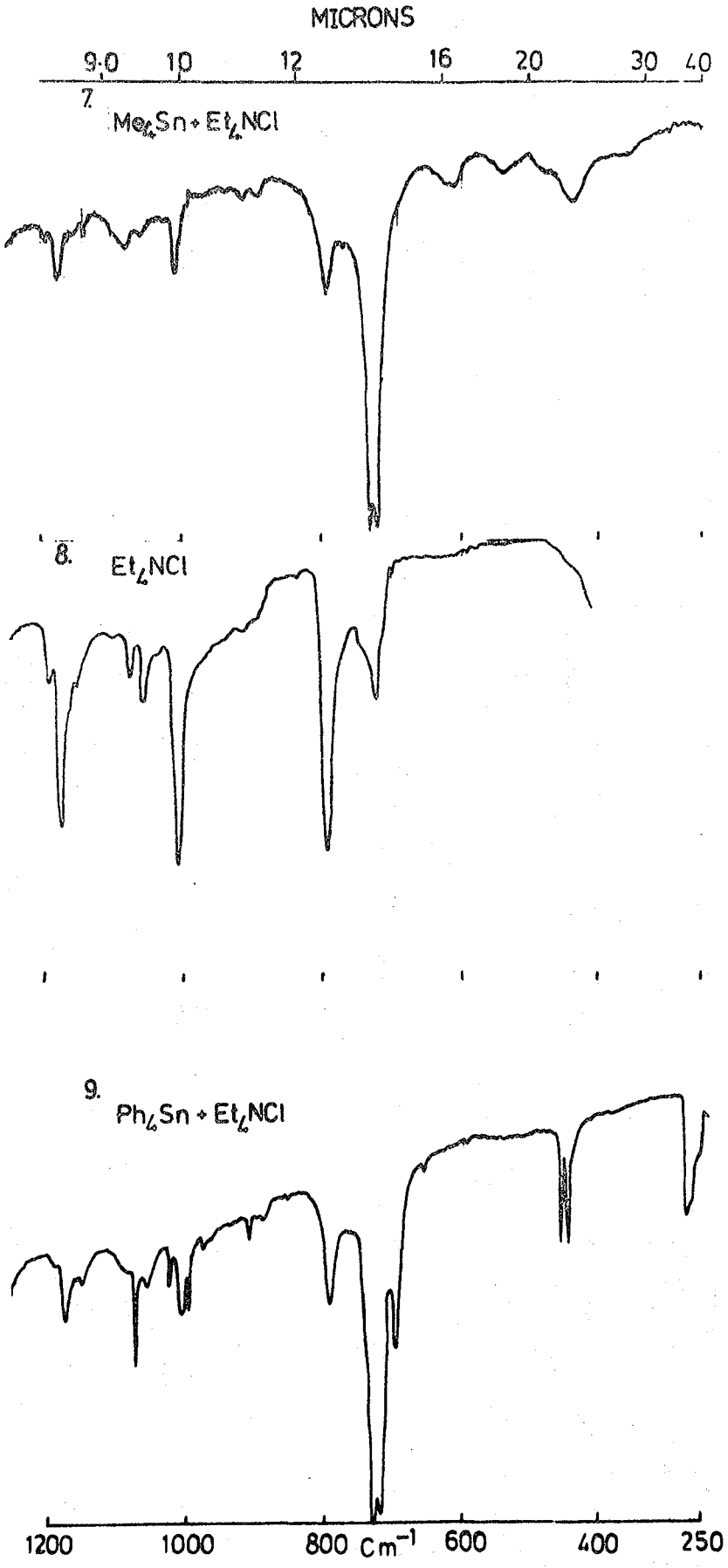
The present work has shown that ^{119}Sn n.m.r. is an invaluable probe in investigating the chemistry of tin-containing species. There is also considerable scope for future work in these fields, particularly for study of unstable and reacting systems, exemplified by the work on reactions with acidic solvents.

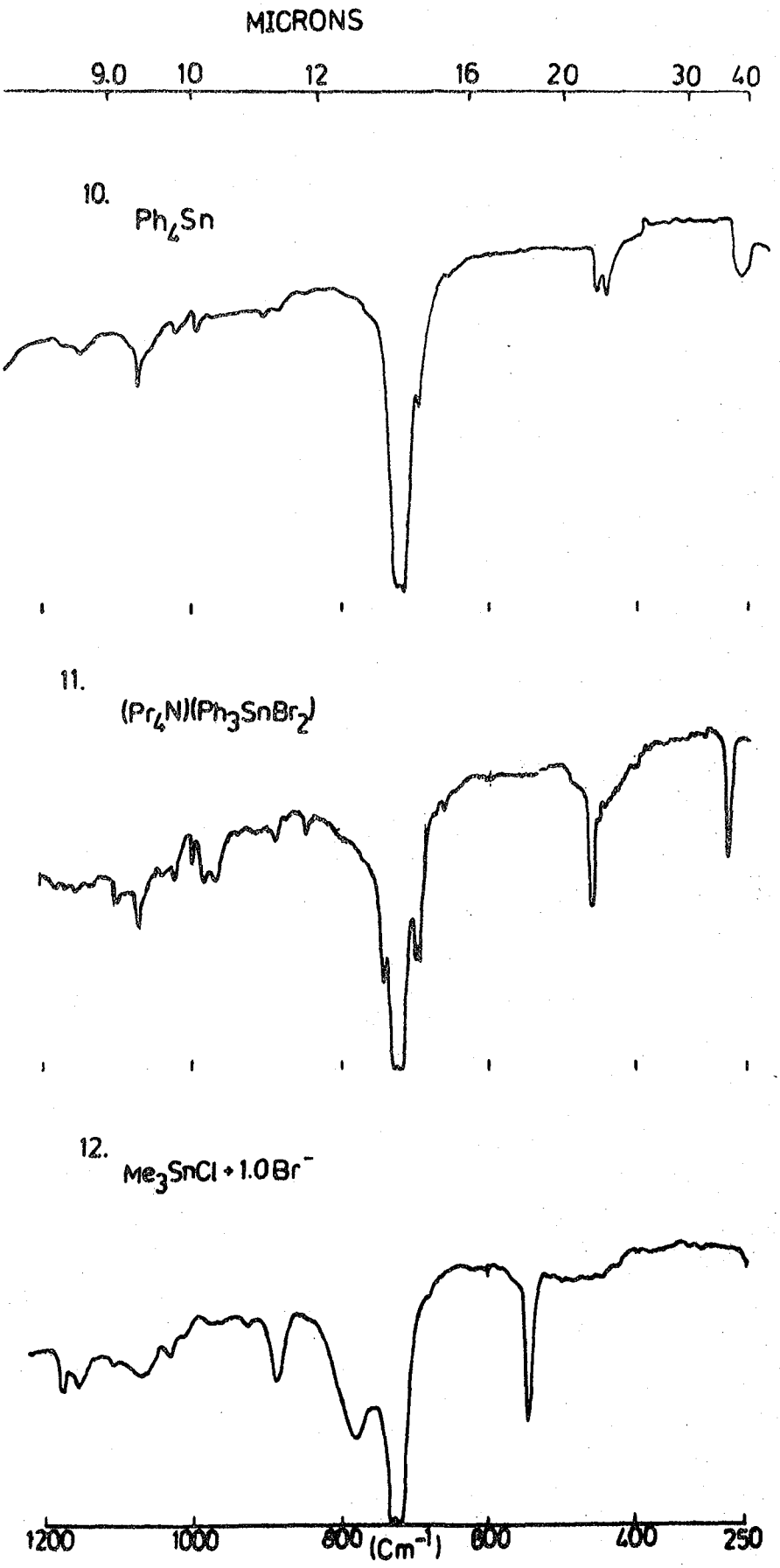
Appendix 1 INFRA-RED SPECTRA OF PRODUCTS REFERRED TO IN THIS THESIS

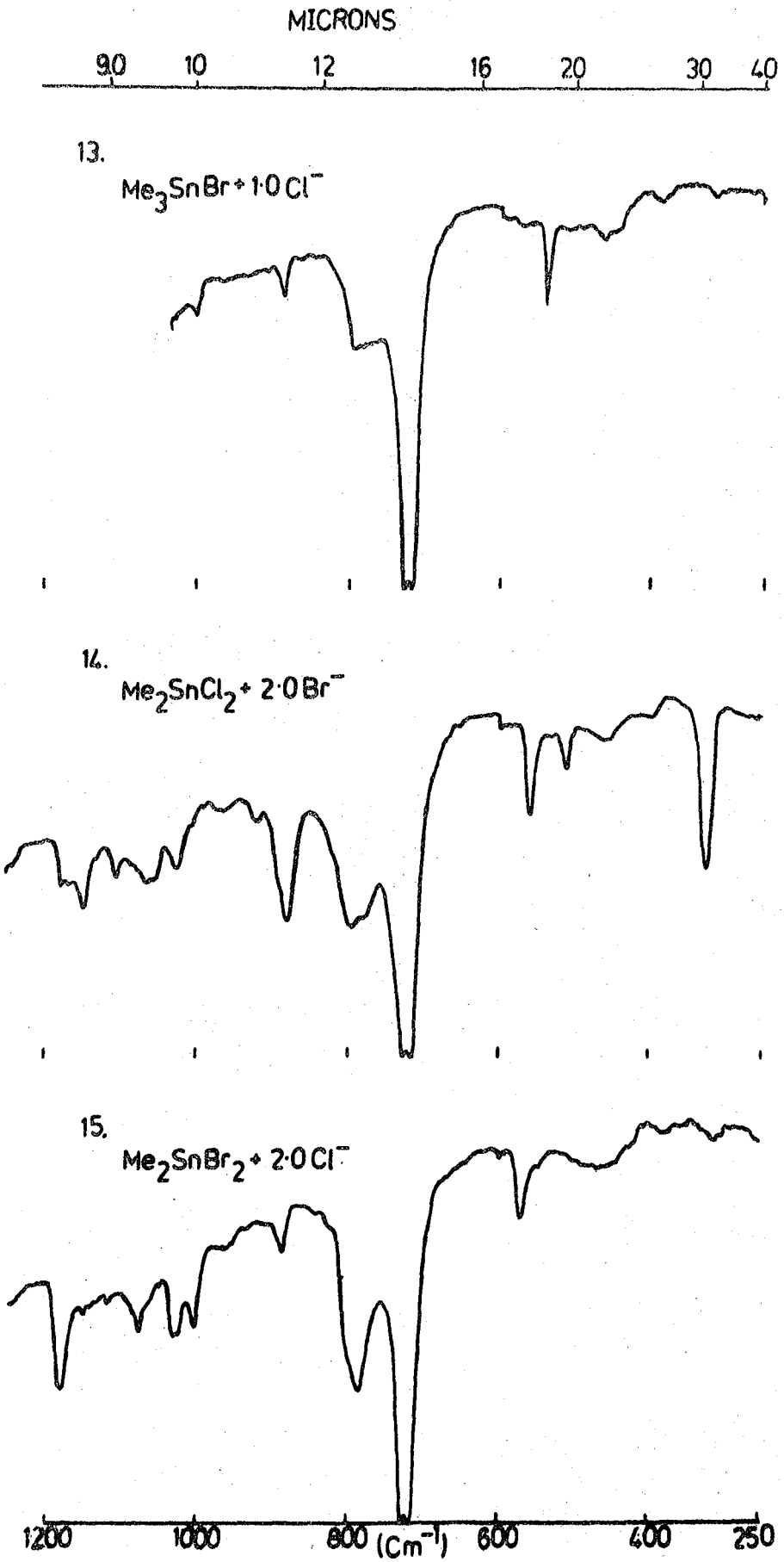
Index No.	Compound/System	Index No.	Compound/System
1	$(Et_4N)(Me_3SnCl_2)$	20	$Me_2SnCl_2 + SbCl_5$
2	$(Et_4N)_2(Me_2SnCl_4)$	21	$MeSnCl_3 + SbCl_5$
3	$(Et_4N)_2(MeSnCl_5)$	22	$Ph_4Sn + SbCl_5$
4	$(Et_4N)(Ph_3SnCl_2)$	23	$Me_4Sn + SbCl_5$
5	$(Pe_4N)_2(Ph_2SnCl_4)$	24	$MeSnCl_3.py_2$
6	$(Pe_4N)_2(PhSnCl_5)$	25	$MeSnCl_3.dipy$
7	$2Et_4NCl + Me_4Sn$	26	$MeSnCl_3.phen$
8	Et_4NCl	27	$Me_2SnCl_2.py_2$
9	$2Et_4NCl + Ph_4Sn$	28	$Me_2SnCl_2.dipy$
10	Ph_4Sn	29	$Me_2SnCl_2.phen$
11	$(Pr_4N)(Ph_3SnBr_2)$	30	$Me_3SnCl.py$
12	$Me_3SnCl + 1.0Br^-$	31	$PhSnCl_3.py_2$
13	$Me_3SnBr + 1.0Cl^-$	32	$PhSnCl_3.dipy$
14	$Me_2SnCl_2 + 2.0Br^-$	33	$PhSnCl_3.phen$
15	$Me_2SnBr_2 + 2.0Cl^-$	34	$Ph_2SnCl_2.py_2$
16	$Ph_3SnCl + SbCl_5$	35	$Ph_2SnCl_2.dipy$
17	$Ph_2SnCl_2 + SbCl_5$	36	$Ph_2SnCl_2.phen$
18	$PhSnCl_3 + SbCl_5$	37	$Ph_3SnCl.py$
19	$Me_3SnCl + SbCl_5$		

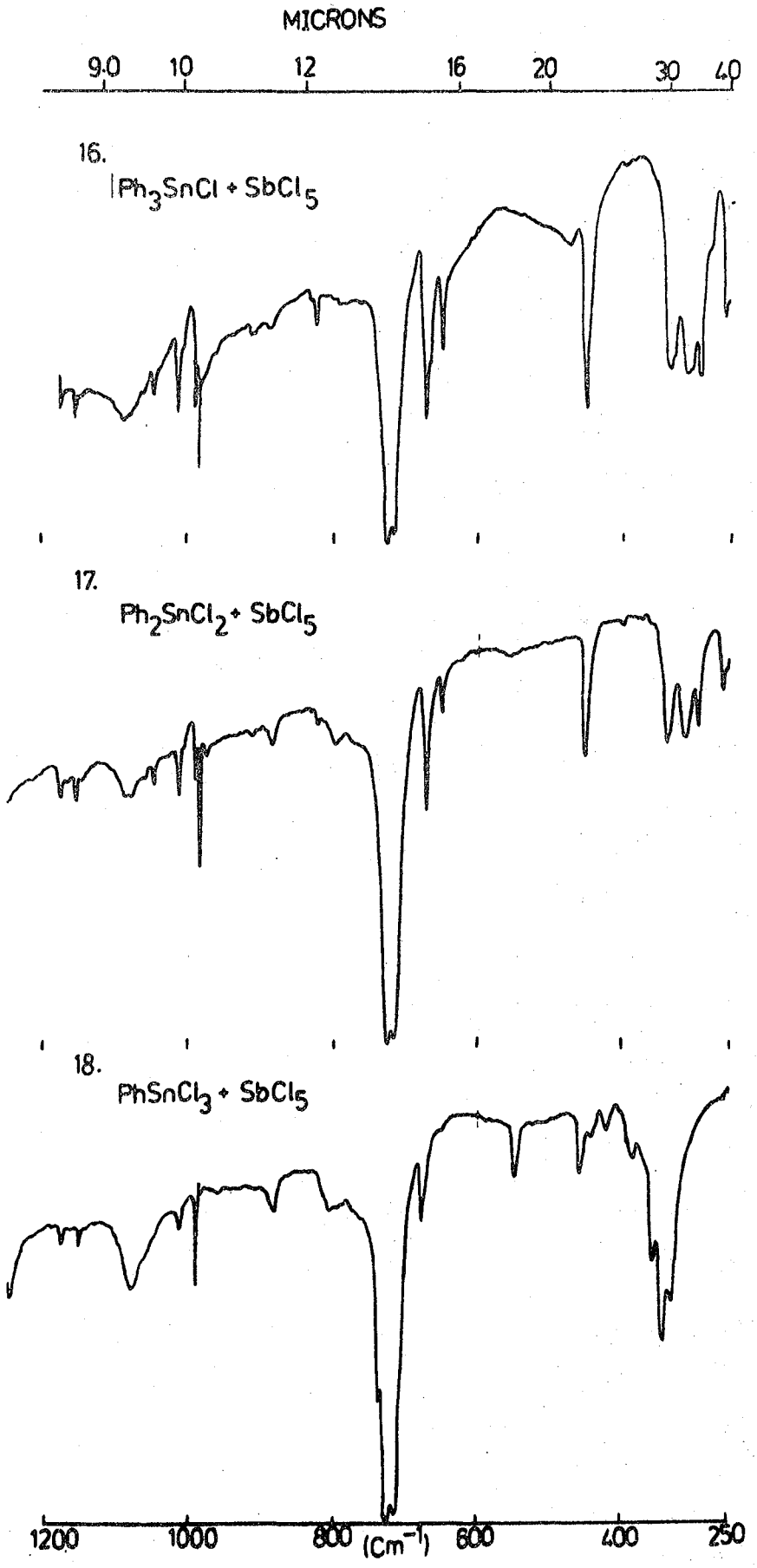

MICRONS
9.0
10
12
16
20
30
40
1.
$(Et_4N)(Me_3SnCl_2)$
2.
$(Et_4N)_2(Me_2SnCl_4)$
3.
$(Et_4N)_2(MeSnCl_5)$
1200
1000
800
(Cm^{-1})
600
400
250

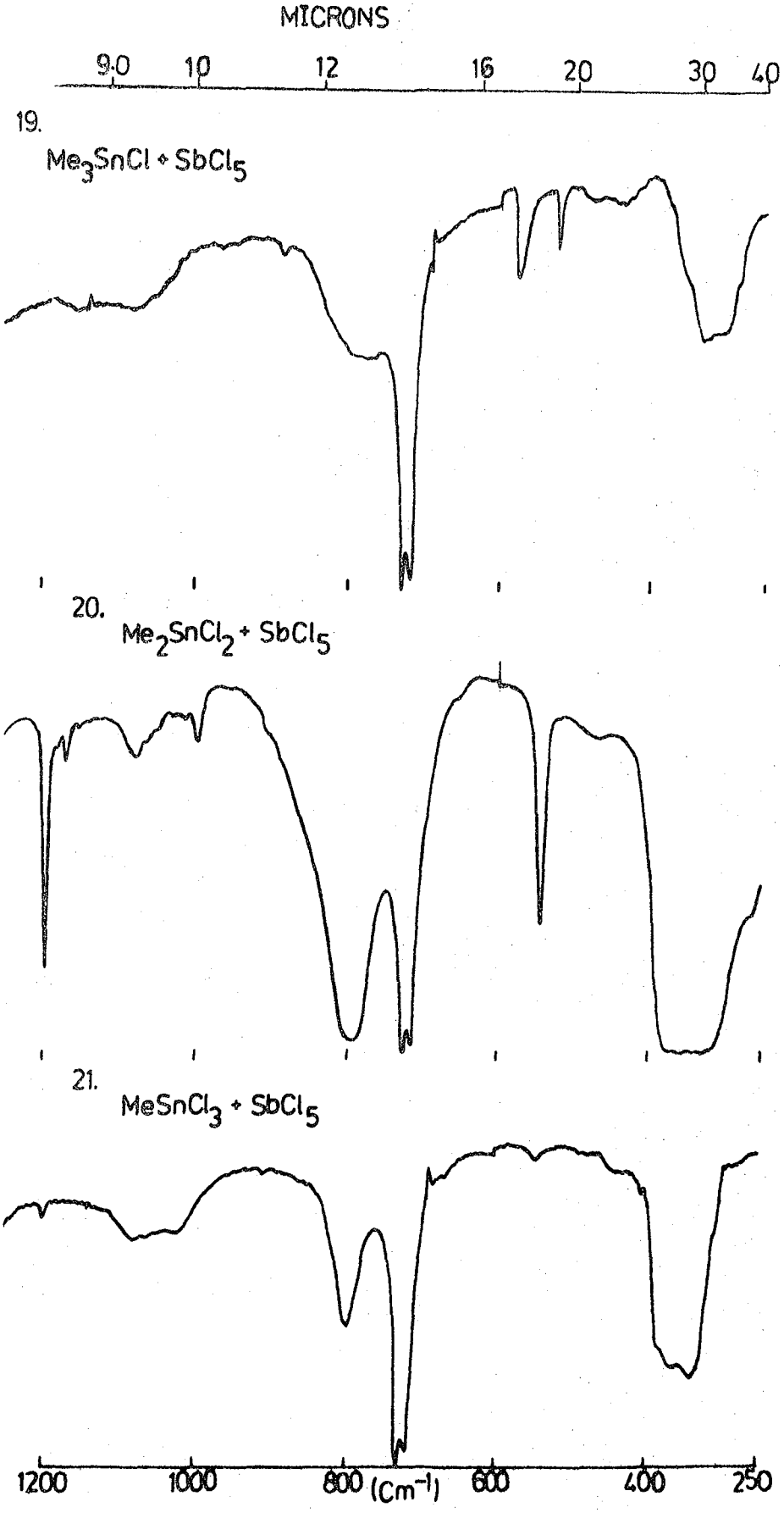

MICRONS
9·0
10
12
16
20
30
40
4.
$(Et_4N)(Ph_3SnCl_2)$
5.
$(Et_4N)_2(Ph_2SnCl_4)$
6.
$(Pe_4N)_2(PhSnCl_5)$
1200
1000
800
(Cm^{-1})
600
400
250

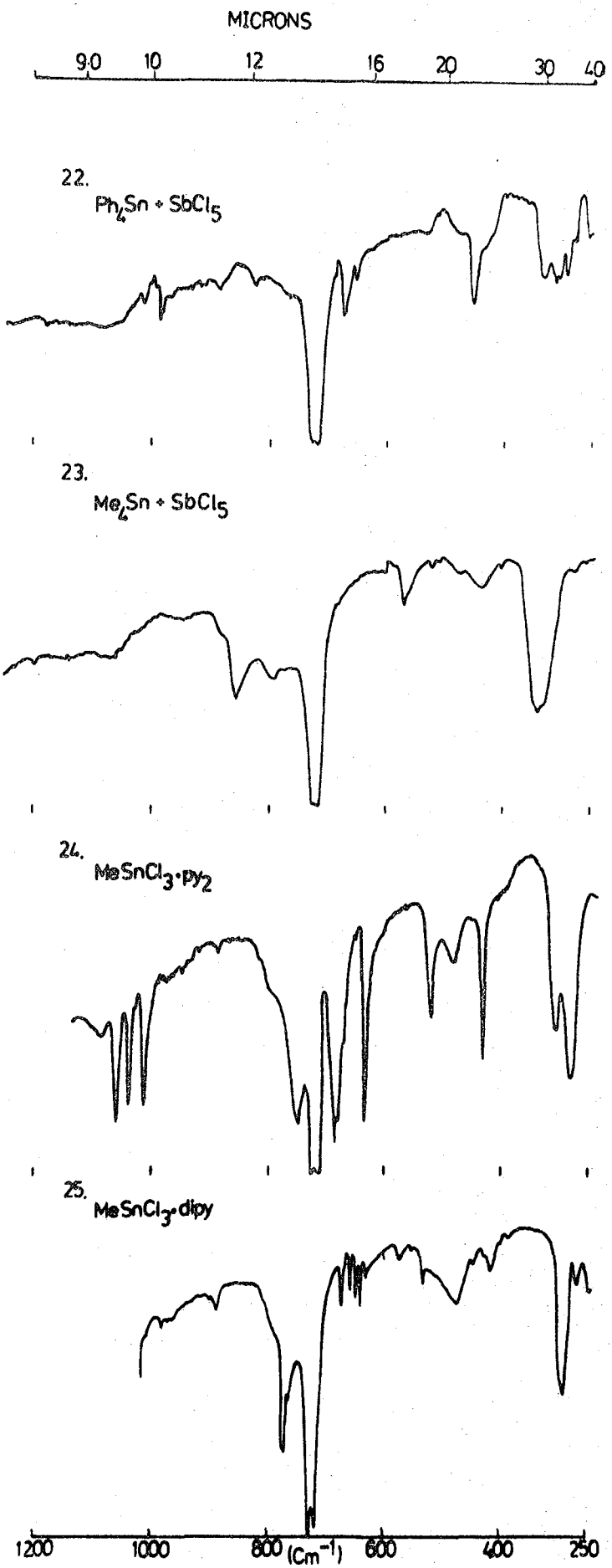

MICRONS
9·0
10
12
16
20
30
40
7.
Me4Sn + Et4NCl
8.
Et4NCl
9.
Ph4Sn + Et4NCl
1200
1000
800
Cm-1
600
400
250

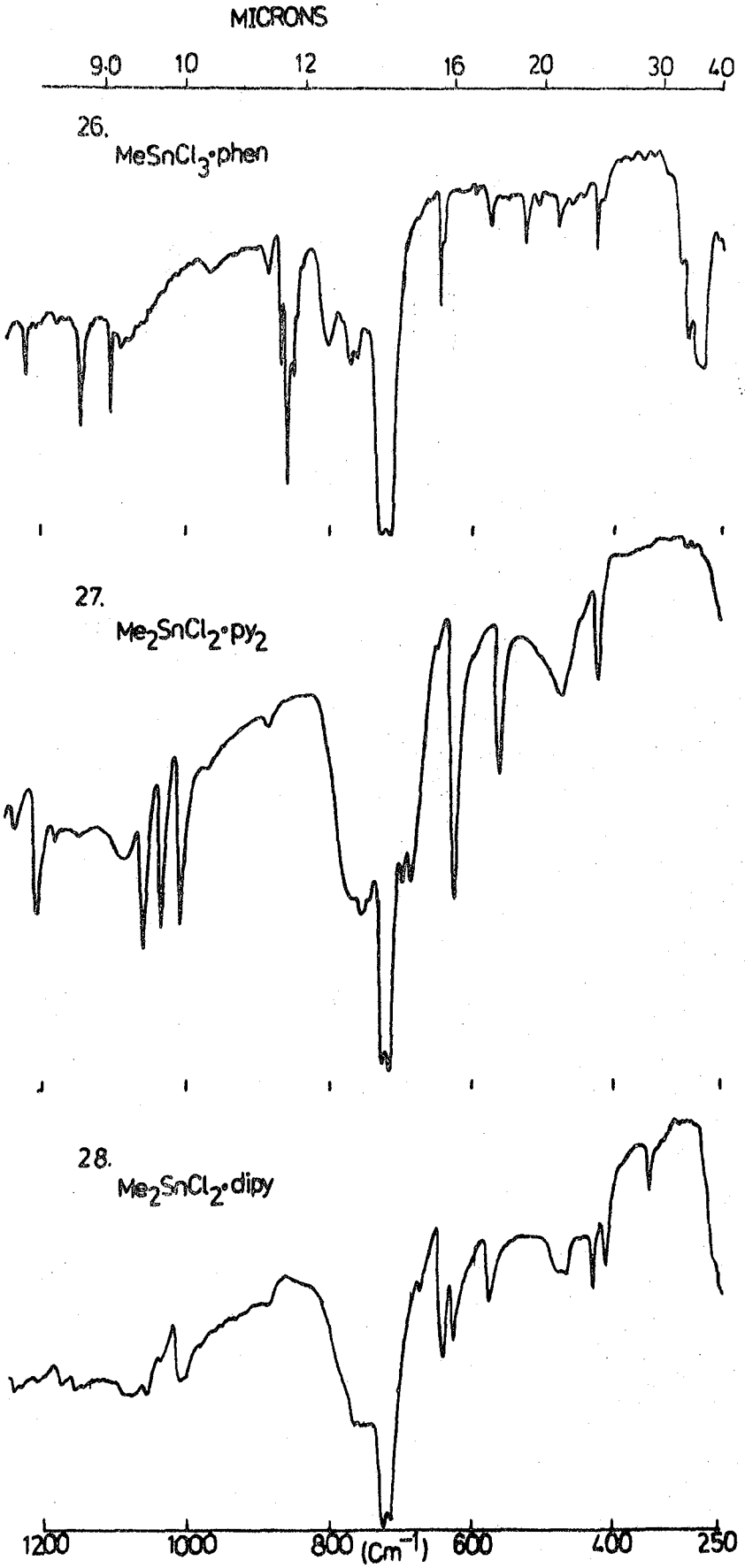

MICRONS
9.0
10
12
16
20
30
40
10.
Ph_4Sn
11.
$(Pr_4N)(Ph_3SnBr_2)$
12.
$Me_3SnCl + 1.0\,Br^-$
1200
1000
800
(Cm^{-1})
600
400
250

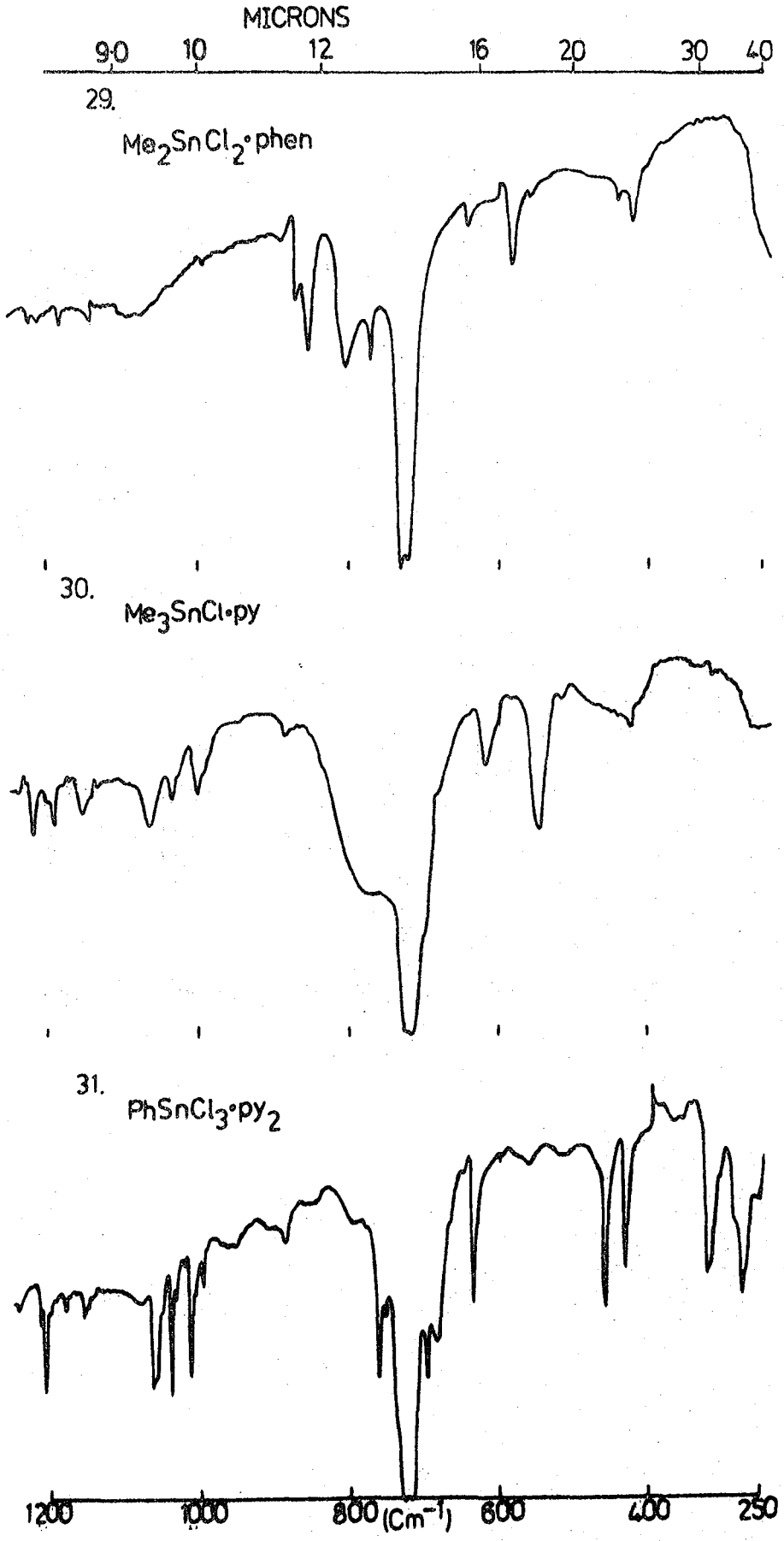

MICRONS
9.0
10
12
16
20
30
40
13.
$Me_3SnBr + 1{\cdot}0\,Cl^-$
14.
$Me_2SnCl_2 + 2{\cdot}0\,Br^-$
15.
$Me_2SnBr_2 + 2{\cdot}0\,Cl^-$
1200
1000
800
(Cm^{-1})
600
400
250

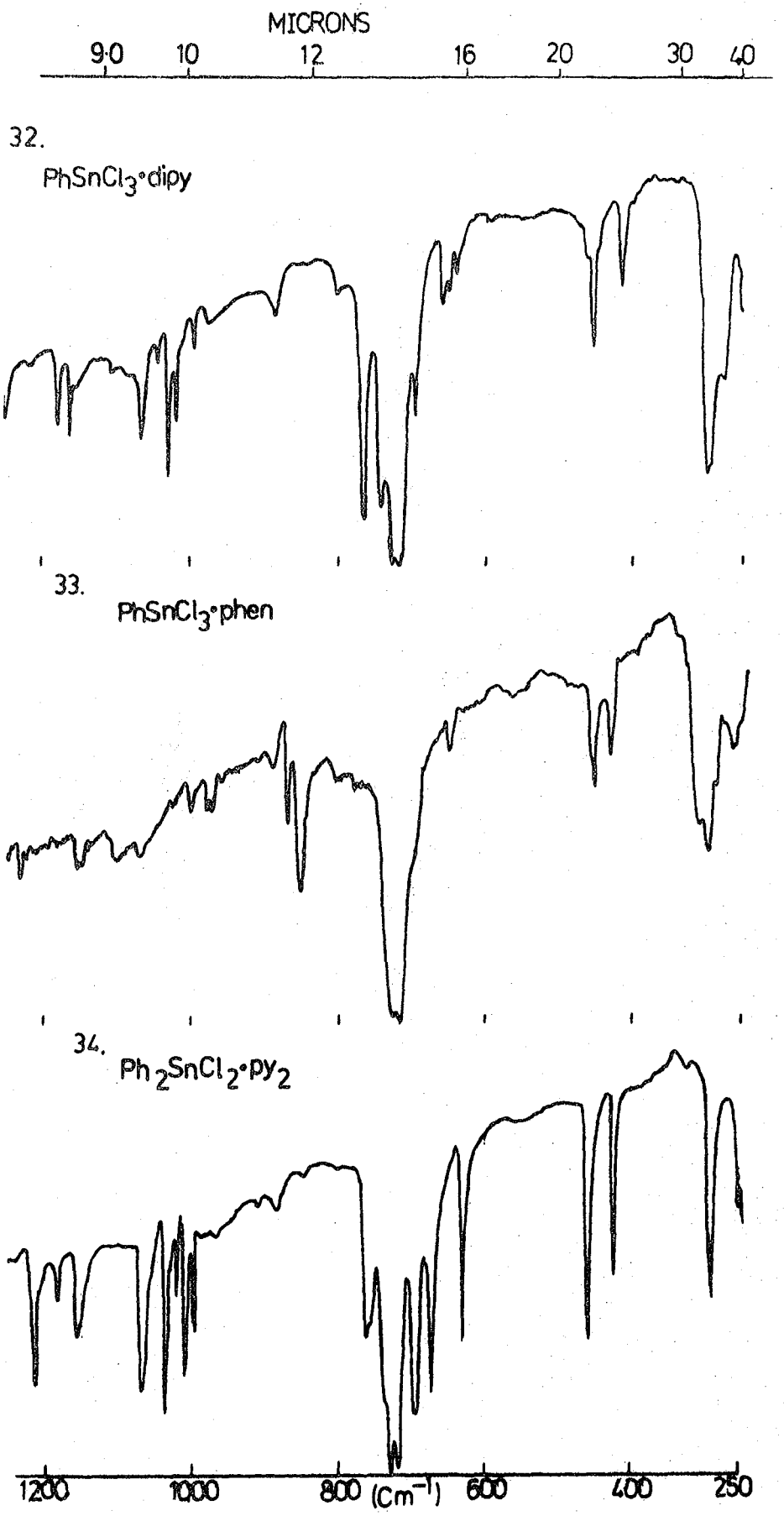

MICRONS
9.0
10
12
16
20
30
40
16.
Ph3SnCl + SbCl5
17.
Ph2SnCl2 + SbCl5
18.
PhSnCl3 + SbCl5
1200
1000
800
(Cm-1)
600
400
250


MICRONS
9.0
10
12
16
20
30
40
19.
$Me_3SnCl + SbCl_5$
20.
$Me_2SnCl_2 + SbCl_5$
21.
$MeSnCl_3 + SbCl_5$
1200
1000
800
(Cm⁻¹)
600
400
250


MICRONS
9.0
10
12
16
20
30
40
22.
$Ph_4Sn + SbCl_5$
23.
$Me_4Sn + SbCl_5$
24.
$MeSnCl_3 \cdot py_2$
25.
$MeSnCl_3 \cdot dipy$
1200
1000
800
(Cm^{-1})
600
400
250


MICRONS
9.0
10
12
16
20
30
40
26.
MeSnCl3·phen
27.
Me2SnCl2·py2
28.
Me2SnCl2·dipy
1200
1000
800
(Cm-1)
600
400
250


MICRONS
9·0
10
12
16
20
30
40
29.
$Me_2SnCl_2 \cdot phen$
30.
$Me_3SnCl \cdot py$
31.
$PhSnCl_3 \cdot py_2$
1200
1000
800
(Cm⁻¹)
600
400
250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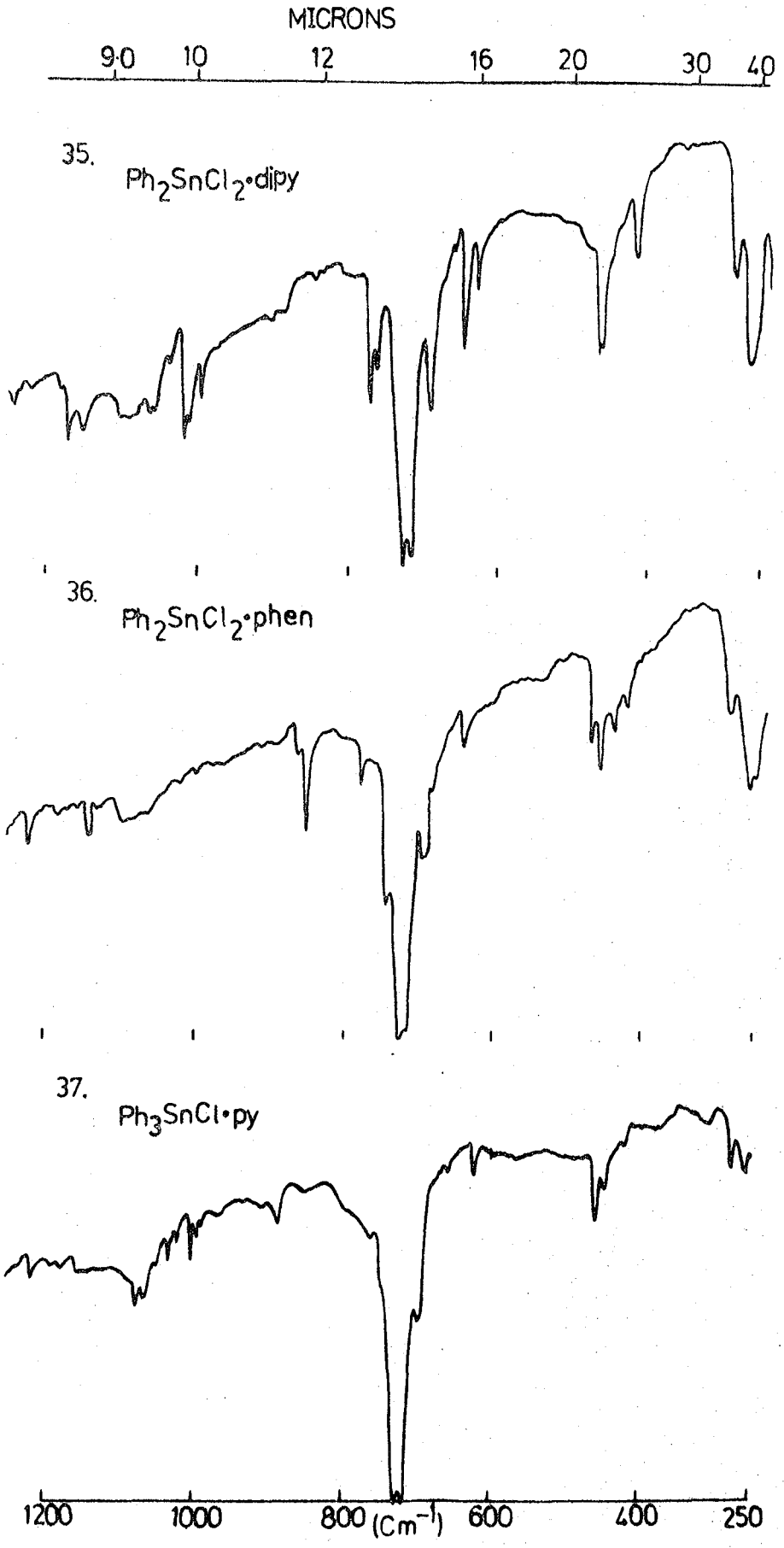
10
12
16
20
30
40
32.
PhSnCl3·dipy
33.
PhSnCl3·phen
34.
Ph2SnCl2·py2
1200
1000
800
(Cm⁻¹)
600
400
250


MICRONS
9·0
10
12
16
20
30
40
35.
Ph_2SnCl_2·dipy
36.
Ph_2SnCl_2·phen
37.
Ph_3SnCl·py
1200
1000
800
(Cm^{-1})
600
400
250

Appendix 2 RAMAN SPECTRA OF PRODUCTS (150 - 650 cm^{-1})

No.	Product	Spectrum
1	$(Et_4N)(Me_3SnCl_2)$	∿150 (s), 178 (m), 390 (vw), 510 (vs), 543 (s).
2	$(Et_4N)_2(Me_2SnCl_4)$	196 (m), 310 (vw), 393 (vw), 513 (vs).
3	$(Et_4N)_2(MeSnCl_5)$	160 (w), 187 (w), 314 (m), 395 (w), 516 (m), 537 (w).
4	$(Et_4N)(Ph_3SnCl_2)$	196 (m), 234 (s), 276 (vw), 418 (w), 619 (w).
5	$(Pe_4N)(Ph_2SnCl_4)$	240 (w), 650 (w).
6	$(Pe_4N)_2(PhSnCl_5)$	161 (vw), 258 (w), 312 (vw).
7	$2Et_4NCl + Me_4Sn$	425 (s).
8	$2Et_4NCl + Ph_4Sn$	157 (m), 213 (s), 265 (w), 425 (w), 617 (w).
9	$(Pr_4N)(Ph_3SnBr_2)$	213 (s), 276 (vw), 307 (vw), 617 (vw).
10	$MeSnCl_3.py_2$	217 (m), 308 (w), 497 (s), 520 (w).
11	$MeSnCl_3$.dipy	174 (m), 245 (vw), 268 (vw), 292 (w), 510 (w), 535 (w).
12	$MeSnCl_3$.phen	422 (vw), 530 (vw).
13	$Me_2SnCl_2.py_2$	219 (m), 426 (vw), 500 (vs), 636 (vw).
14	Me_2SnCl_2.dipy	168 (m), 188 (m), 237 (m), 417 (vw), 510 (s), 634 (vw), 647 (w).
15	Me_2SnCl_2.phen	162 (s), 196 (m), 238 (m), 281 (w), 422 (m), 480 (vw), 528 (vs).
16	Me_3SnCl.py	∿160 (w,br.), ∿250 (w,br.), 517 (s), 550 (w).
17	$PhSnCl_3.py_2$	167 (vw), 185 (vw), 222 (w), 259 (s), 318 (m), 430 (vw), 640 (vw).
18	$PhSnCl_3$.dipy	254 (w), 297 (w).
19	$PhSnCl_3$.phen	∿206 (vw,br.), 269 (w), 303 (w), 428 (w).
20	$Ph_2SnCl_2.py_2$	194 (w), 245 (s), 622 (vw), 640 (vw).

No.	Product	Spectrum
21	Ph_2SnCl_2.dipy	203 (vw), 215 (w), 234 (vw), 263 (m), 359 (vw).
22	Ph_2SnCl_2.phen	151 (vw), 175 (vw), 213 (w), 262 (w), 284 (vw).
23	Ph_3SnCl.py	no bands 150 - 650 cm^{-1}.

The Raman spectra of all organotin chloride starting materials (with the exception of Me_4Sn) are listed in Table 5, Chapter 1.

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